

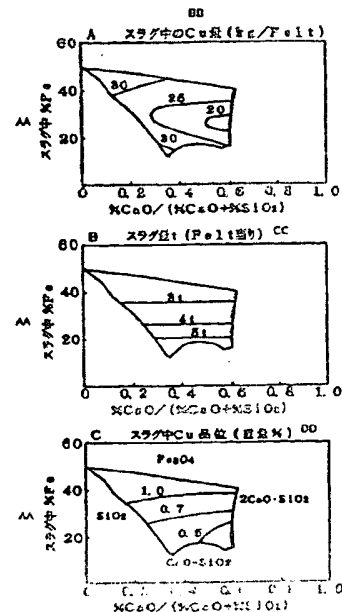
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(54) Title: METHOD FOR SMELTING COPPER SULFIDE CONCENTRATE  (54) 発明の名称 硫化銅精鉱の熔錬方法  (57) Abstract A method for smelting copper sulfide concentrate wherein a copper sulfide concentrate is subjected to oxidation smelting to thereby remove most part of Fe in the concentrate to a slag and at the same time remove a part or most part of S as SO <sub>2</sub> , and a white regulus, a matte similar to a white regulus, or a crude metal of copper is obtained, characterized in that a SiO <sub>2</sub> source and CaO source are added to the above copper sulfide concentrate and the oxidation smelting is carried out in a manner such that a slag having a weight ratio CaO/(SiO <sub>2</sub> + CaO) of 0.3 to 0.6 and a weight ratio Fe/(FeO <sub>x</sub> + SiO <sub>2</sub> + CaO) of 0.2 to 0.5, and a white regulus, a matte similar to a white regulus, or a crude metal of copper are formed.		



AA... Fe % IN SLAG  
 BB... AMOUNT OF Cu IN SLAG (KG / Fe 1 TON)  
 CC... AMOUNT OF SLAG (PER TON OF Fe)  
 DD... CONTENT OF Cu IN SLAG (WT %)

## (57)要約

硫化銅精鉱を酸化熔錬し、該硫化銅精鉱中のFeの大部分をスラグに除去するとともに、Sの一部もしくは大部分をSO<sub>2</sub>として除去し、硫化銅精鉱中の銅を白カワあるいは白カワに近いマットあるいは粗銅として得る方法において、前記硫化銅精鉱に溶剤としてSiO<sub>2</sub>源とCaO源とを加え、CaO/(SiO<sub>2</sub>+CaO)の重量比が0.3~0.6で、かつFe/(FeO<sub>x</sub>+SiO<sub>2</sub>+CaO)の重量比が0.2~0.5であるスラグと、白カワあるいは白カワに近いマットあるいは粗銅とを生成するように酸化熔錬する。

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## 明 細 書

硫化銅精鉱の熔錬方法

## 技術分野

本発明は、銅の乾式製錬法に関し、特に、硫化銅精鉱あるいは硫化銅精鉱から得られたマットを酸化熔錬して白カワあるいは粗銅を得る製錬方法に関する。

## 背景技術

従来、銅の溶融製錬は、硫化銅精鉱を酸化溶融し、鉱石中のFeの一部を酸化しスラグとして除去するとともに、Sの一部をSO<sub>2</sub>とし、CuをFeSとCu<sub>2</sub>Sの混合物であるマットとして濃縮するマット熔錬工程、次いで、得られたマットをさらに酸化してFeをスラグとして除去し、Feをほとんど含まない白カワ(Cu<sub>2</sub>S)を得る白カワ製造工程、この白カワをさらに酸化して粗銅を得る造銅工程からなる。マット熔錬炉としては一般的に自熔炉が用いられ、白カワ製造工程と造銅工程は、通常、転炉で行われる。

通常、硫化銅精鉱には脈石分としてSiO<sub>2</sub>が含まれるため、マット熔錬工程では鉄シリケートスラグが用いられる。転炉でも、通常、溶剤として珪酸鉱を添加して鉄シリケートスラグを形成する。

マット熔錬炉では、マット中の銅品位(マットグレード; MG)が、通常70重量%以下のマットを製造し、これを転炉に導入する。転炉はバッチ式で、前述のように、白カワ、次いで粗銅とする。プラント全体の生産性を高めるうえで、マット熔錬炉のMGを高め、バッチ式転炉の負荷を下げるのが望ましい。マット熔錬炉で白カワまで酸化できれば、転炉での白カワ製造工程が不要になる。さらに、粗銅まで酸化できれば、転炉工程そのものが不要となる。しかし、マット熔錬炉の酸化度を上げようとする、鉄シリケートスラグに起因する以下の問題があった。

(1) マグネタイトトラブル：

鉄シリケートスラグでは3価のFeの溶解度が低い。このため、固体マグネタイトが析出して炉底に沈積するなど、いわゆるマグネタイトトラブルを招く。これを避けるために、MGを高くする場合には、熔錬温度を1300℃以上に上げざるを得ない。しかし、これは炉体の損傷を促進する。また、銅の一部を酸化してスラグ中の銅品位を高くすると、鉄シリケートスラグでもマグネタイトトラブルを避けて粗銅が得られるが、このときのスラグ中の銅品位は25%以上必要で、粗銅の収率が著しく低くなる。

(2) 銅の酸化溶解：

MGの上昇とともに、鉄シリケートスラグ中への銅の酸化物としての溶解度が著しく上昇する。

(3) 不純物の濃縮：

鉄シリケートスラグとマットあるいは粗銅の共存下では、As、Sbなどの酸化物の鉄シリケートスラグへの溶解度が低いために、これらの不純物がマットあるいは粗銅中に濃縮する。その程度は、鉄シリケートスラグと粗銅が共存する場合、特に著しく、これらの不純物の高い硫化銅精鉱から鉄シリケートスラグ共存下で直接粗銅を得ることができない理由の一つとされていた。

これらの点から、鉄シリケートスラグを用いるマット熔錬炉では、通常、MG 65～70%程度を上限として操業が行われている。

また、同様の問題からマットをS品位の低い粗銅にまで酸化する工程においては、鉄シリケートスラグ共存下では連続化が不可能とされ、通常、転炉を用いたバッチ式の処理が行われてきた。鉄シリケートスラグ共存下で、マットから粗銅を連続的に得ている報告（特開昭58-224128号）もあるが、これはスラグ-白カワ-粗銅の3相共存下で粗銅を得たもので、このときの粗銅中のS品位は1.5%と高くならざるを得ず、後工程である精製炉の操業負荷を著しく増大させる。

この問題を避けて、本願発明者の一人は、マット熔錬炉で白カワを製造する方法を特公平5-15769号で提案している。これは、溶剤として石灰を加え、硫化銅精鉱中の鉄分をカルシウムフェライトスラグとして除去するというもので

ある。カルシウムフェライトスラグを用いることで、マグネタイトの析出は防止でき、また、As、Sbなどの不純物のスラグへの除去率は、鉄シリケートスラグより高いという利点があった。しかし、下記のような問題があった。

(1) 硫化銅精鉱中には、通常、若干のSiO<sub>2</sub>が含まれる。このため、なるべく純粋なカルシウムフェライトスラグを生成させるためには、処理する硫化銅精鉱はSiO<sub>2</sub>品位の低いもの(3%以下)に限られる。

(2) 上記の低SiO<sub>2</sub>硫化銅精鉱であっても、カルシウムフェライトスラグ中に少量のSiO<sub>2</sub>が存在すると、スラグの粘性を悪化させたり、泡立ちを引き起こし、安定的な操炉が困難であった。このため、カルシウムフェライトスラグを用いる場合、スラグ中のSiO<sub>2</sub>品位は1%以下(スラグ中のFeに対し重量で約1.7%以下)に制御しなければならず、この方法により、カルコパイライトを主体とした標準的な硫化銅精鉱から白カワを得ようとする場合、実用上は硫化銅精鉱中のSiO<sub>2</sub>品位は0.4%以下に限定されていた。

(3) カルシウムフェライトスラグへのPbの溶解度が低いため、Pbが該スラグ中に分配されにくく、白カワに濃縮する。

(4) カルシウムフェライトスラグへの銅の酸化物としての溶解量が多く、選鉱による回収率が低い。

一方、転炉工程では、マットをさらに酸化して白カワ、粗銅とするうえで、鉄シリケートスラグに起因する問題を避けるために、工程をバッチとし、白カワとスラグが共存する状態でいったん吹錬を中断して炉を傾転させてスラグを排出し、白カワのみを転炉内に残して粗銅までの酸化を行う。この方式は、バッチ方式に起因する種々の不利益を含んでおり、転炉操業を煩雑なものとしている。

三菱連続製銅法では、転炉(C炉)工程でカルシウムフェライトスラグを用いることでマグネタイトの析出を避け、MG65%程度のマットから粗銅を連続的に製造している。しかし、カルシウムフェライトスラグに起因する以下のような問題があった。

(1) スラグ中の銅品位は酸素分圧に対して連続的に変化し、粗銅中のS品位を下げるほどスラグ中の銅品位が高くなる。実用上は、粗銅中のSを0.5~1%程度でスラグ中のCuは13~15%となり、これ以下のS品位とするのは銅の

収率の点から効率的ではない。

(2) カルシウムフェライトスラグ中の銅分は、主として酸化物で化学的に溶解したものであり、徐冷しても選鉱による銅の回収率が低い。

(3) 前述のように、カルシウムフェライトスラグ中の $\text{SiO}_2$ が1～3%程度になると粘性が著しく増大し、フォーミング（泡立ち）を起こす。このため、鉄シリケートスラグの混入したマットは原料として使用困難であった。マット中のFe品位を10%とすると、マット中への混入が許容できる $\text{SiO}_2$ はマットに対して0.2%以下であり、マット熔錬工程から産出されるマットへのスラグの混入防止に特に注意する必要があった。

(4) Pbの溶解度が低いため、Pbがスラグ中に分配されにくく、粗銅に濃縮する。このため、高Pb原料から従来の方法で電解可能なアノードの製造は困難であった。

(5) 同一温度で比較した場合、煉瓦への浸透性が大きいため、シリケートスラグより転炉煉瓦の浸食性が大きい。

#### 発明の開示

本発明の目的は、硫化銅精鉱あるいはマットを連続的に酸化して白カワあるいは粗銅を得るうえで、(1) 1300℃以下の通常の銅熔錬温度でマグネタイトラブルがなく、(2)  $\text{SiO}_2$ を含有する硫化銅精鉱やマットの処理にも適用でき、(3) スラグへの銅の損失が少なく、(4) 浮選によりスラグ中の銅分の回収が可能で、(5) As、Sb、Pbのスラグへの除去能が高く、(6) 煉瓦の熔損が少ない硫化銅精鉱の熔錬方法を提供することにある。

本発明の方法は、硫化銅精鉱に溶剤として $\text{SiO}_2$ 源とCaO源を加え、 $\text{CaO}/(\text{SiO}_2+\text{CaO})$ の重量比が0.3～0.6で、かつ $\text{Fe}/(\text{FeO}_x+\text{SiO}_2+\text{CaO})$ の重量比が0.2～0.5であるスラグと白カワに近いマットあるいは白カワあるいは粗銅とを生成するように酸化熔錬することを特徴とする。

また、硫化銅精鉱を熔錬して得られるマットに $\text{SiO}_2$ 源とCaO源を加え、

$\text{CaO} / (\text{SiO}_2 + \text{CaO})$  の重量比が 0.3～0.6 で、かつ  $\text{Fe} / (\text{FeO}_x + \text{SiO}_2 + \text{CaO})$  の重量比が 0.2～0.5 であるスラグと粗銅とを生成するように酸化熔錬することを特徴とする。

#### 図面の簡単な説明

図1： 硫化銅精鉱を酸化してMG75のマットを得る場合の、1300℃でのスラグ中の銅量(A)、生成するスラグ量(B)、スラグ中の銅品位(C)をスラグ中の $\text{CaO} / (\text{SiO}_2 + \text{CaO})$ 比(横軸)およびFe%(縦軸)に対して示したグラフである。

図2： スラグ中のAsの活量係数をスラグ組成に対して示したグラフである。

図3： スラグ中のPbの活量係数をスラグ組成に対して示したグラフである。

図4： 白カワ共存下でS品位1～1.5%程度の粗銅を得る場合の、1300℃でのスラグ中の銅量(A)、生成するスラグ量(B)、スラグ中の銅品位(C)をスラグ中の $\text{CaO} / (\text{SiO}_2 + \text{CaO})$ 比(横軸)およびFe%(縦軸)に対して示したグラフである。

図5： 1573Kにおいて、溶銅共存下でスラグに酸化溶解する銅濃度と酸素分圧の関係を示すグラフである。

#### 発明を実施するための最良の形態

白カワあるいは粗銅を製造する高い酸素分圧条件におけるスラグの特徴を、従来、銅製錬で用いられてきた鉄シリケートスラグ、三菱法で用いられているカルシウムフェライトスラグ、本発明で用いる鉄カルシウムシリケートスラグとを、比較して表1に示す。

表 1

	鉄シリケート スラグ	カルシウムフェラ イトスラグ	鉄カルシウムシリ ケートスラグ
粘性が低い	×	○	○
マット、粗銅の 懸垂が少ない	×	○	○
銅の酸化溶解が 少ない	×	×	○
銅の硫化溶解が 少ない	○	×	×
Pbの溶解度が 高い	○	×	○
As, Sb 溶解度	×	○	○
Mg 初溶溶解度	×	○	○
煉瓦の熔損が 少ない	○	×	○

従来、鉄シリケートスラグに若干のCaOを加えて粘性を改善することは行われてきた。ただし、マット熔錬工程ではCaO品位が高くなると、銅の硫化物としての溶解度が増えるうえに、スラグ量も増えるので不利と考えられてきた。しかし、硫化溶解が問題とならない白カワや粗銅と共存する条件下では、鉄シリケートスラグやカルシウムフェライトスラグで銅の酸化溶解が著しく多くなるのに対し、本発明で用いる鉄カルシウムシリケートスラグでは、銅の酸化溶解が少なく済むため、スラグ量×銅品位＝酸化溶解による銅の損失量で評価すると、従来法（鉄シリケートスラグあるいはカルシウムフェライトスラグを用いる高MGのマット熔錬法や白カワ熔錬や直接製銅法）より少なくなることを見出し、本発明に至った。



図1は、硫化銅精鉱を酸化してMG75のマットを得る場合の、1300℃でのスラグ中の銅量(A)、生成するスラグ量(B)、スラグ中の銅品位(C)を、スラグ中の $\text{CaO}/(\text{SiO}_2 + \text{CaO})$ の重量比(横軸)およびFe%(縦軸)に対して示したグラフである。各図には、各固相の飽和線が示されており、 $\text{CaO}/(\text{SiO}_2 + \text{CaO})$ の重量比が0.6以上では $2\text{CaO} \cdot \text{SiO}_2$ が析出する。また、Fe品位が高すぎると、マグネタイトが析出する。図の左端が従来の鉄シリケートスラグ( $\text{CaO}=0\%$ )に相当する。

スラグ中の鉄品位が低くなるほど銅品位が低くなる傾向にあり、また $\text{CaO}/(\text{SiO}_2 + \text{CaO})$ の重量比が大きいほど銅品位は低くなる。生成するスラグ量は、スラグ中の鉄品位によって決まり、除去すべき鉄量は原料により決まるので、スラグ中の鉄品位が高いほどスラグ量は少なくなる。スラグへ移行する銅量(損失量)は、スラグ量×スラグ中銅品位で決まり、最上段に示したように、 $\text{CaO}/(\text{SiO}_2 + \text{CaO})$ の重量比が0.5~0.6、そして、 $\text{Fe}/(\text{FeO} + \text{SiO}_2 + \text{CaO})$ の重量比が0.2~0.5の組成付近で極小値をもつ。すなわち、スラグ中への銅の損失を最小にするという点からは、この付近の組成のスラグを選べばよい。

一方、図2は、スラグ中のAsの活量係数をスラグ組成に対して示したグラフである。横軸に $\text{CaO}/(\text{SiO}_2 + \text{CaO})$ の重量比、縦軸にAsの活量係数( $\gamma_{\text{AsO}1.5}$ )を示している。図の左端が従来の鉄シリケートスラグ、右端がカルシウムフェライトスラグに相当し、本発明で用いる鉄カルシウムシリケートスラグは両者の中間に位置する。活量係数は、値が小さいほど、その元素がスラグ中に除去されやすいことを示す。

図2より、 $\text{CaO}/(\text{SiO}_2 + \text{CaO})$ の重量比を0.3以上にすると、Asの除去能は、鉄シリケートスラグより高くなることがわかる。なお、Asと同じV族に属するSbも同様の挙動を示す。

一方、図3に示したように、Pbは逆の挙動を示し、Pbの活量係数( $\gamma_{\text{PbO}}$ )がカルシウムフェライトスラグで著しく大きな値となっており、 $\text{CaO}/(\text{SiO}_2 + \text{CaO})$ の重量比が小さなほど小さな値を示す。Pbの除去能は、 $\text{CaO}/(\text{SiO}_2 + \text{CaO})$ の重量比が0.3~0.6では、鉄シリケートス

ラグと比べるとやや劣るものの、カルシウムフェライトslagに比べると、かなり大きな除去能をもっている。

以上より、 $\text{CaO} / (\text{SiO}_2 + \text{CaO})$  の重量比を 0.3 ~ 0.6 とすることで、As、Sb、Pb のいずれについてもslag中に除去しやすくなることがわかる。

図4は、図1と同様の関係を、白カワ共存下でS品位1~1.5%程度の粗銅を得る場合について示したものである。図の左端が鉄シリケートslag ( $\text{CaO} = 0\%$ )、右端がカルシウムフェライトslag ( $\text{SiO}_2 = 0\%$ ) に相当する。最上段の図より、銅の損失量は、 $2\text{CaO} \cdot \text{SiO}_2$  の飽和線に近いところで極小をとることがわかる。カルシウムフェライトslagでも、銅の損失量は比較的小さいが、少量の $\text{SiO}_2$  が持ち込まれると、 $2\text{CaO} \cdot \text{SiO}_2$  飽和となり、slagの泡立ちという問題を生ずる。

不純物の分配については、マット熔錬と同じ傾向にあり、カルシウムフェライトslagはPbを吸収しにくく、鉄シリケートslagではAs、Sbを吸収しにくいという欠点があるのに対し、 $\text{CaO} / (\text{SiO}_2 + \text{CaO})$  の重量比を 0.3 ~ 0.6 とすることで、As、Sb、P のいずれをもslag中に除去しやすくなる。

以上より、 $\text{CaO} / (\text{SiO}_2 + \text{CaO})$  の重量比が 0.3 ~ 0.6、 $\text{Fe} / (\text{FeO}_x + \text{SiO}_2 + \text{CaO})$  の重量比が 0.2 ~ 0.5 の範囲に銅の損失を最小にし、かつPb、As、Sbのいずれをも除去しやすい最適組成があることがわかる。

図5は、酸素分圧に対するslag中の銅品位を示したもので、図4に示した場合より、さらに酸化度が高い領域でS品位の低い粗銅を得ようとする場合の挙動が示されている。図中、曲線Aが鉄シリケートslag、曲線Dがカルシウムフェライトslag、曲線B、Cが本発明で用いる鉄カルシウムシリケートslagを示す。鉄シリケートslag、カルシウムフェライトslagでは、酸素分圧の上昇に応じてslag中の銅は100%まで連続的に変化する。それに対して、鉄カルシウムシリケートslagでは、銅品位約20%で酸化銅飽和となるので、slag中の銅品位はこの品位以上には上がらない。すなわち、この条件で粗銅を作ると、

スラグ中の銅品位が約20%でS品位が0.01%以下の粗銅（酸化銅飽和の粗銅）が得られる。同程度の酸化度の粗銅を鉄シリケートスラグあるいはカルシウムフェライトスラグで作ると、スラグ中の銅品位は著しく高くなり収率の点から実用とはならない。

煉瓦の浸食については、スラグ成分の煉瓦への浸透が大きな影響を及ぼすと考えられている。通常、銅製錬で用いられるマグクロ煉瓦中にスラグ成分が浸透した場合、スラグ中の酸化鉄はペリクレース（ $MgO$ ）や $Cr_2O_3$ を含むスピネルに吸収されることが知られている。 $SiO_2$ を含むスラグの場合、煉瓦内に浸入すると、酸化鉄がペリクレース（ $MgO$ ）やスピネル中に固溶することにより、スラグ中の $SiO_2$ 濃度が高くなる。その結果、スラグの粘性が上昇し、それ以上のスラグ浸透が抑制されると考えられる。

以下に実施例を説明する。

〔実施例1〕

1300℃に保持されたマグネシア製ルツボ内に表2に示す熔融マット40gと熔融スラグ60gを用意し、熔融浴中に同じく表2に示す組成の硫化銅精鉱と $SiO_2$ （ $SiO_2$ 純分95%以上）と $CaO$ （ $CaO$ 純分98%以上）とをランスパイプを用いて95% $O_2$ －5% $N_2$ （容量%）とともに、ランスパイプを浸漬せずに、吹き込んだ。

表2

（重量%）

	Cu	Fe	S	$SiO_2$	CaO
熔融マット	74.8	2.0	20.5	-	-
熔融スラグ	2.4	35.1	-	22.9	16.2
硫化銅精鉱	31.4	24.0	30.2	6.9	-

吹き込みに用いたランスパイプはアルミナ製で、20 g/分の硫化銅精鉱と、1.94 g/分の $\text{SiO}_2$ 、2.20 g/分の $\text{CaO}$ を4.5リットル/分の95% $\text{O}_2$ －5% $\text{N}_2$ （容量%）ガスとともに吹き込んだ。

上記の条件で吹き込みを50分間継続して、10分間静止した後、冷却凝固させて、マットおよびスラグの重量ならびに分析品位を求め、最初に装入したマット、スラグの量ならびに品位から各成分量を差し引いて、反応により生成したマット量、スラグ量ならびにその品位を計算した結果を表3に示す。

表3

（重量%）

	産出重量 (g)	Cu	Fe	S	$\text{SiO}_2$	$\text{CaO}$
生成マット	375	76.2	1.0	20.1	-	-
生成スラグ	641	1.9	35.0	-	23.8	16.0

## 〔実施例2〕

1300℃に保持されたマグネシア製ルツボ内に表4に示す組成の熔融粗銅30gと熔融スラグ80gを用意し、熔融浴中に同じく表4に示す組成の硫化銅精鉱と $\text{SiO}_2$ （ $\text{SiO}_2$ 純分95%以上）と $\text{CaO}$ （ $\text{CaO}$ 純分98%以上）とをランスパイプを用いて95% $\text{O}_2$ －5% $\text{N}_2$ （容量%）とともに、ランスパイプを浸漬せずに、吹き込んだ。

表 4

(重量%)

	Cu	Fe	S	SiO <sub>2</sub>	CaO
熔融粗銅	97.5	-	1.2	-	-
熔融スラグ	3.8	31.0	-	26.1	18.2
硫化銅精鉱	31.4	24.0	30.2	6.9	-

吹き込みに用いたランスパイプはアルミナ製で、20 g/分の硫化銅精鉱と、3.02 g/分のSiO<sub>2</sub>、2.88 g/分のCaOを5.8リットル/分の95%O<sub>2</sub>-5%N<sub>2</sub>（容量%）ガスとともに吹き込んだ。

上記の条件で吹き込みを50分間継続して、10分間静止した後、冷却凝固させて、粗銅およびスラグの重量ならびに分析品位を求め、最初に装入した粗銅、スラグの量ならびに品位から各成分量を差し引いて、反応により生成した粗銅量、スラグ量ならびにその品位を計算した結果を表5に示す。

表 5

(重量%)

	産出重量 (g)	Cu	Fe	S	SiO <sub>2</sub>	CaO
生成粗銅	273	98.1	-	0.99	-	-
生成スラグ	764	4.2	29.8	-	26.3	17.9

## 【実施例 3】

1300℃に保持されたマグネシア製ルツボ内に表6に示す組成の熔融粗銅6

0 g と熔融スラグ 40 g を用意し、熔融浴中に同じく表 6 に示す組成のマットと  $\text{SiO}_2$  ( $\text{SiO}_2$  純分 95 % 以上) と  $\text{CaO}$  ( $\text{CaO}$  純分 98 % 以上) とを 95 %  $\text{O}_2$  - 5 %  $\text{N}_2$  (容量%) とともに、ランスパイプを浸漬せずに、吹き込んだ。

表 6

(重量%)

	Cu	Fe	S	$\text{SiO}_2$	$\text{CaO}$
熔融粗銅	97.5	-	1.2	-	-
熔融スラグ	18.4	25.3	-	22.1	13.5
マット	65.3	9.7	21.4	-	-

吹き込みに用いたランスパイプはアルミナ製で、20 g/分の硫化銅精鉱と、1.78 g/分の  $\text{SiO}_2$  と、1.14 g/分の  $\text{CaO}$  とを 4.0 リットル/分の 95 %  $\text{O}_2$  - 5 %  $\text{N}_2$  (容量%) ガスとともに吹き込んだ。

上記の条件で吹き込みを 50 分間継続して、10 分間静止した後、冷却凝固させて、粗銅およびスラグの重量ならびに分析品位を求め、最初に装入した粗銅、スラグの量ならびに品位から各成分量を差し引いて、反応により生成した粗銅量、スラグ量ならびにその品位を計算した結果を表 7 に示す。

表 7

(重量%)

	産出重量 (g)	Cu	Fe	S	SiO <sub>2</sub>	CaO
生成粗銅	558	98.8	-	0.05	-	-
生成スラグ	382	20.6	24.9	-	20.8	14.0

この実施例 1～3 の試験において、ダスト発生率は 4～7 重量%の範囲であった。この間、マグネタイトの発生によるトラブルは全くなかった。

## [実施例 4]

実施例 3 において生成したスラグを 200 メッシュアンダーが 95%となるまでボールミルにて微粉碎し、このスラグ 200 g を水で 65 重量%スラリーとし、試験用浮選機によって浮選テストを実施した。この際、起泡剤としてバイン油 0.02 g、浮選剤として市販の DM-2000、MCB-4、ザンセートを各々 0.006 g、0.01 g、0.03 g 添加した。

テスト結果を表 8 に示す。浮選により 80%以上の銅を回収できることが確認された。

表 8

原鉱	精鉱		尾鉱	
Cu%	Cu%	分布	Cu%	分布
20.8	38	81	1.5	19

## [実施例 5]

反応塔の内径 1.5 m、高さ 3.5 m、セトラー部の内径 1.5 m、長さ 5.

2 mの小型自熔炉を用い、表9に示した組成の精鉱と粉珪石と粉石灰（いずれも200  $\mu\text{m}$ 以下に粉碎したもの）を所定の比率で調合、乾燥したもの（以下、乾鉱という）を反応塔天井に設けられた精鉱バーナーから酸素50%の酸素富化空気とともに反応塔内に吹き込み、スラグとマットを得た。精鉱バーナーには重油バーナーが組み込まれており、反応塔の熱バランスを保つように重油量を調節した。操業は4日間行った。得られた結果を表9に示す。表9より、MG約76の高品位マットが安定的に得られたことがわかる。

表9

(重量%)

		物量 (kg/h)	Cu	Fe	S	SiO <sub>2</sub>	CaO
処理	硫化銅精鉱	1040	31.4	25.1	30.2	6.9	-
	珪石	104	-	2	-	95	
	石灰石	208	-	-	-	-	53
産出	熔融マット	382	76.8	1.0	20.1	-	-
	熔融スラグ	700	2.5	35.0	-	24.2	16.1

精鉱バーナー送風空気量580 Nm<sup>3</sup>/h、酸素濃度50%、

重油量53リットル/h、

生成スラグ平均温度1258℃、生成マット平均温度1146℃

#### [比較例1]

1300℃に保持されたマグネシア製ルツボ内に表10に示す組成の熔融マット30gと熔融スラグ40gを用意し、熔融浴中に同じく表10に示す組成の硫化銅精鉱とSiO<sub>2</sub>（SiO<sub>2</sub>純分97%以上）とを95%O<sub>2</sub>-5%N<sub>2</sub>（容量



%)とともに、ランスパイプを浸漬せずに、吹き込んだ。

表 1 0

(重量%)

	Cu	Fe	S	SiO <sub>2</sub>	CaO
熔融マット	76.3	2.8	20.8	-	-
熔融スラグ	5.0	42.0	-	30.0	-
硫化銅精鉱	30.3	29.1	33.5	1.8	-

吹き込みに用いたランスパイプはアルミナ製で、37.5 g/分の硫化銅精鉱と、7.6 g/分のSiO<sub>2</sub>とを9.2リットル/分の95%O<sub>2</sub>-5%N<sub>2</sub> (容量%)ガスとともに吹き込んだ。

試験開始5分後には、マットと生成マグネタイトの混合した高融点物質の形成により、供給原料の融体中への吹き込みが不可能となり、さらにこれらの物質のため、ランスパイプの閉塞が起こり、実験の継続が不可能となった。

#### [比較例2]

1300℃に保持されたマグネシア製ルツボ内に表11に示す組成の熔融粗銅60gと熔融スラグ40gを用意し、熔融浴中に同じく表11に示す組成のマットとCaO (CaO純分98%以上)を95%O<sub>2</sub>-5%N<sub>2</sub> (容量%)とともに、ランスパイプを浸漬せずに、吹き込んだ。

表 1 1

(重量%)

	Cu	Fe	S	SiO <sub>2</sub>	CaO
熔融粗銅	97.5	-	1.2	-	-
熔融スラグ	16.4	47.6	-	-	17.6
マット	64.0	9.5	21.0	2.0	-

吹き込みに用いたランスパイプはアルミナ製で、20 g/分のマットと、0.73 g/分のCaOとを0.20リットル/分の95%O<sub>2</sub>-5%N<sub>2</sub>（容量%）ガスとともに吹き込んだ。

試験開始30分後、スラグのわき上がり現象が起こり、ルツボ内の熔体の大半がルツボ外に吹きこぼれ、実験の継続が不可能となった。

[比較例3]

1300℃に保持されたマグネシア製ルツボ内に表12に示す組成の熔融粗銅60gと熔融スラグ40gを用意し、熔融浴中に同じく表12に示す組成のマットとCaO（CaO純分98%以上）を95%O<sub>2</sub>-5%N<sub>2</sub>（容量%）とともに、ランスパイプを浸漬せずに、吹き込んだ。

表 1 2

(重量%)

	Cu	Fe	S	SiO <sub>2</sub>	CaO
溶融粗銅	97.5	-	1.2	-	-
溶融スラグ	16.4	47.6	-	-	15.7
マット	65.3	9.7	21.4	-	-

吹き込みに用いたランスパイプはアルミナ製で、20 g/分のマットと、0.7 g/分のCaOとを4.2リットル/分の95%O<sub>2</sub>-5%N<sub>2</sub> (容量%) ガスとともに吹き込んだ。

上記の条件で吹き込みを50分間継続して、10分間静止した後、冷却凝固させて粗銅およびスラグの重量ならびに分析品位を求め、最初に装入した粗銅、スラグの量ならびに品位から各成分量を差し引いて、反応により生成した粗銅量、スラグ量ならびにその品位を計算した結果を表13に示す。

S品位0.06%の粗銅が得られたが、スラグ中の銅品位が高く、粗銅の収率は約80%であった。

表 1 3

(重量%)

	産出重量 (g)	Cu	Fe	S	SiO <sub>2</sub>	CaO
生成粗銅	534	98.3	-	0.06	-	-
生成スラグ	290	32.7	32.0	-	-	11.2

## 〔比較例 4〕

Cu 16.4%、Fe 47.6%、CaO 15.7%を含むカルシウムフェライトスラグを200メッシュアンダーが95%となるまでボールミルにて微粉碎し、このスラグ200gを水で65重量%スラリーとし、試験用浮選機にて浮選テストを実施した。この際、起泡剤としてパイン油0.02g、浮選剤として市販のDM-2000、MCB-4、ザンセートを各々0.006g、0.01g、0.03g添加した。

テスト結果を表14に示す。カルシウムフェライトスラグから浮選により銅を回収することは困難であった。

表 1 4

原鉱	精鉱		尾鉱	
Cu%	Cu%	分布	Cu%	分布
16.4	21	54	10	46

## 産業上の利用の可能性

本発明の方法により、硫化銅精鉱あるいはマットを連続的に酸化して白カワあるいは粗銅を得るうえで、マグネタイトトラブルがなく、SiO<sub>2</sub>を含有する硫化銅精鉱やマットの処理にも適用でき、スラグへの銅の損失が少なく、また、浮選によるスラグ中の銅分の回収が可能で、As、Sb、Pbのスラグへの除去能が高く、煉瓦の熔損が少ない硫化銅精鉱の熔錬が行える。

## 請求の範囲

請求項1： 硫化銅精鉱を酸化熔錬し、該硫化銅精鉱中のFeの大部分をスラグに除去するとともに、Sの一部もしくは大部分をSO<sub>2</sub>として除去し、硫化銅精鉱中の銅を白カワあるいは白カワに近いマットあるいは粗銅として得る方法において、前記硫化銅精鉱に溶剤としてSiO<sub>2</sub>源とCaO源とを加え、CaO / (SiO<sub>2</sub> + CaO) の重量比が0.3～0.6で、かつFe / (FeO<sub>x</sub> + SiO<sub>2</sub> + CaO) の重量比が0.2～0.5であるスラグと、白カワあるいは白カワに近いマットあるいは粗銅とを生成するように酸化熔錬することを特徴とする硫化銅精鉱の熔錬方法。

請求項2： 生成したスラグを徐冷固化した後、粉碎して浮選し、回収した銅分を酸化熔錬工程に繰り返すことを特徴とする請求項1に記載の硫化銅精鉱の熔錬方法。

請求項3： 硫化銅精鉱中のSiO<sub>2</sub>含有量が、スラグに除去しようとするFeに対して1.7重量%以上であることを特徴とする請求項1に記載の硫化銅精鉱の熔錬方法。

請求項4： 生成したスラグの温度を1300℃以下に制御することを特徴とする請求項1に記載の硫化銅精鉱の熔錬方法。

請求項5： 硫化銅精鉱を酸化熔錬し、該硫化銅精鉱中のFeの一部およびSの一部をスラグおよびSO<sub>2</sub>に除去して、得られたFeSとCu<sub>2</sub>Sの混合物であるマットを、さらに酸化熔錬してFeおよびSをスラグおよびSO<sub>2</sub>として除去して粗銅を得る方法において、前記マットにSiO<sub>2</sub>源とCaO源とを加え、CaO / (SiO<sub>2</sub> + CaO) の重量比が0.3～0.6で、かつFe / (FeO<sub>x</sub> + SiO<sub>2</sub> + CaO) の重量比が0.2～0.5であるスラグと、粗銅とを生成するように酸化熔錬することを特徴とする硫化銅精鉱の熔錬方法。

請求項6： 生成したスラグを徐冷固化した後、粉碎して浮選し、回収した銅分をマットの酸化熔錬工程に繰り返すことを特徴とする請求項5に記載の硫化銅精鉱の熔錬方法。

請求項7： 生成したスラグを熔融状態のまま、マットの酸化熔錬工程に繰

り返すことを特徴とする請求項 5 に記載の硫化銅精鉱の熔錬方法。

請求項 8 : 生成したスラグを冷却固化した後、マットの酸化熔錬工程に繰り返すことを特徴とする請求項 5 に記載の硫化銅精鉱の熔錬方法。

請求項 9 : マット中の  $\text{SiO}_2$  含有量がスラグ中に除去しようとする  $\text{Fe}$  に対し 1.7 重量%以上であることを特徴とする請求項 5 に記載の硫化銅精鉱の熔錬方法。

請求項 10 : 生成したスラグの温度を  $1300^\circ\text{C}$  以下に制御することを特徴とする請求項 5 に記載の硫化銅精鉱の熔錬方法。

## 図 面

図 1

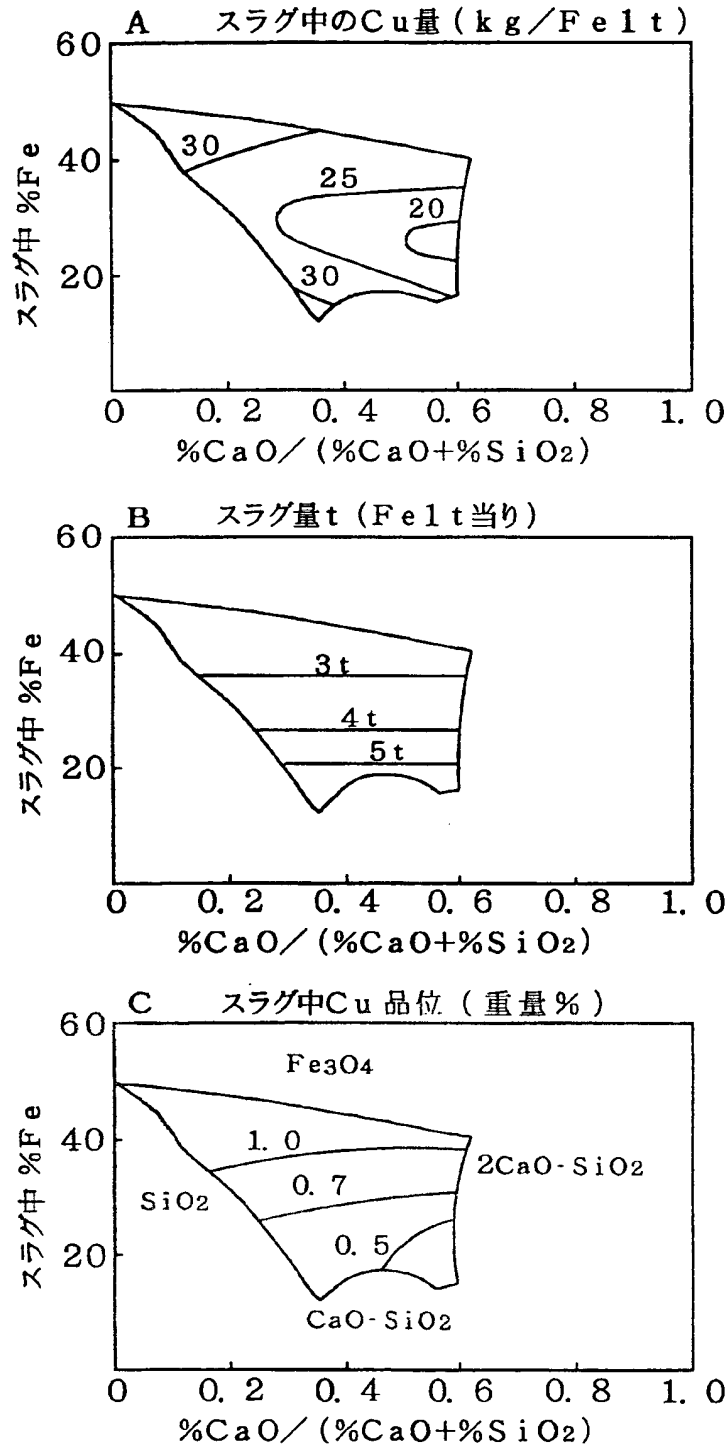


図 2

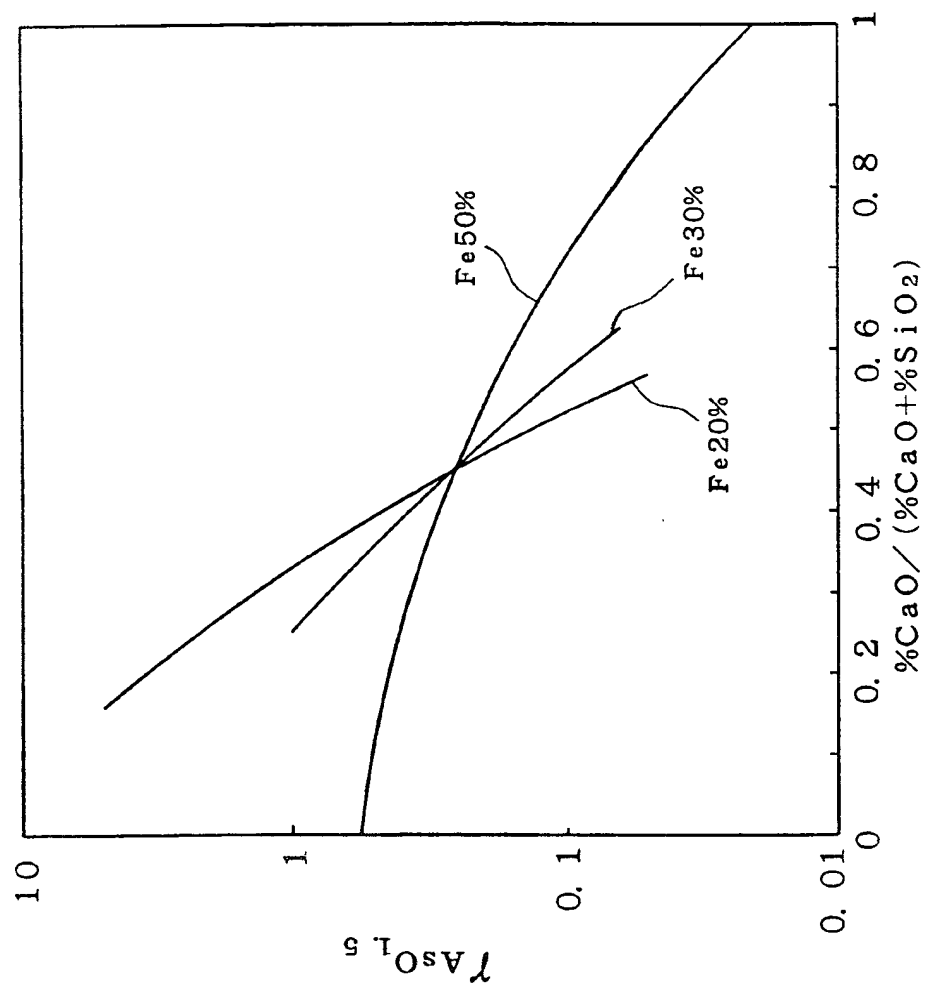




図 3

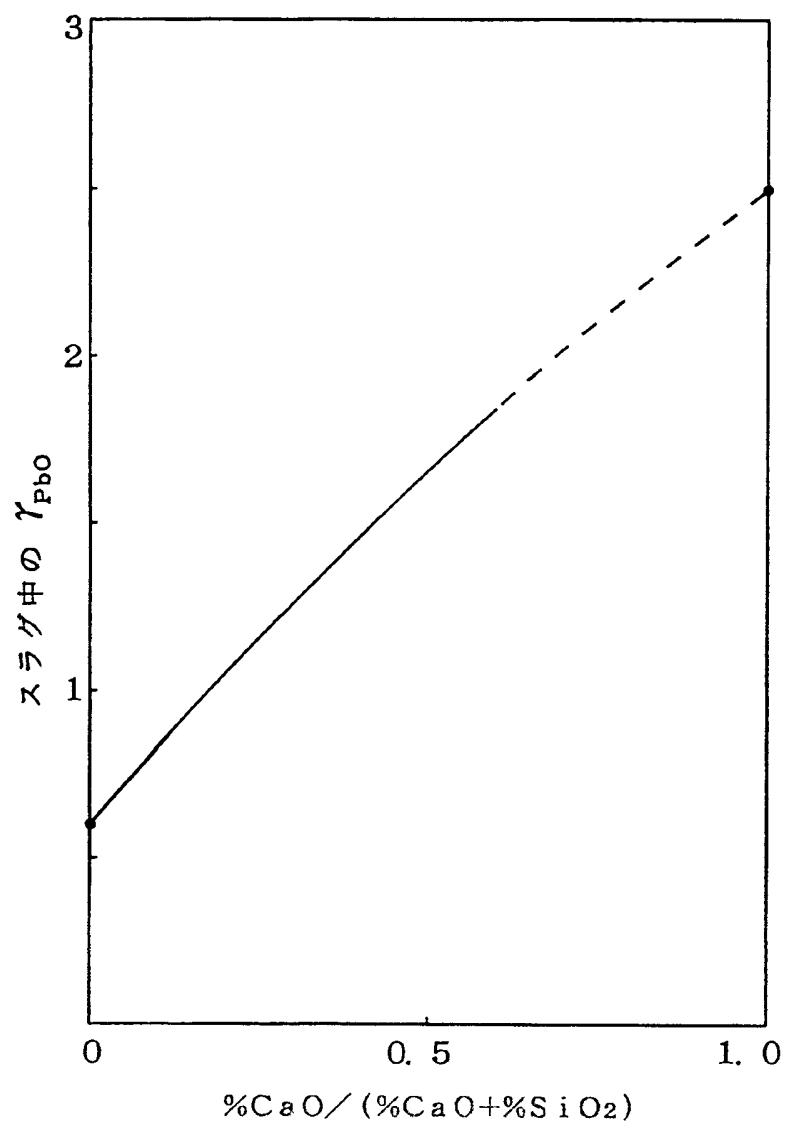


図 4

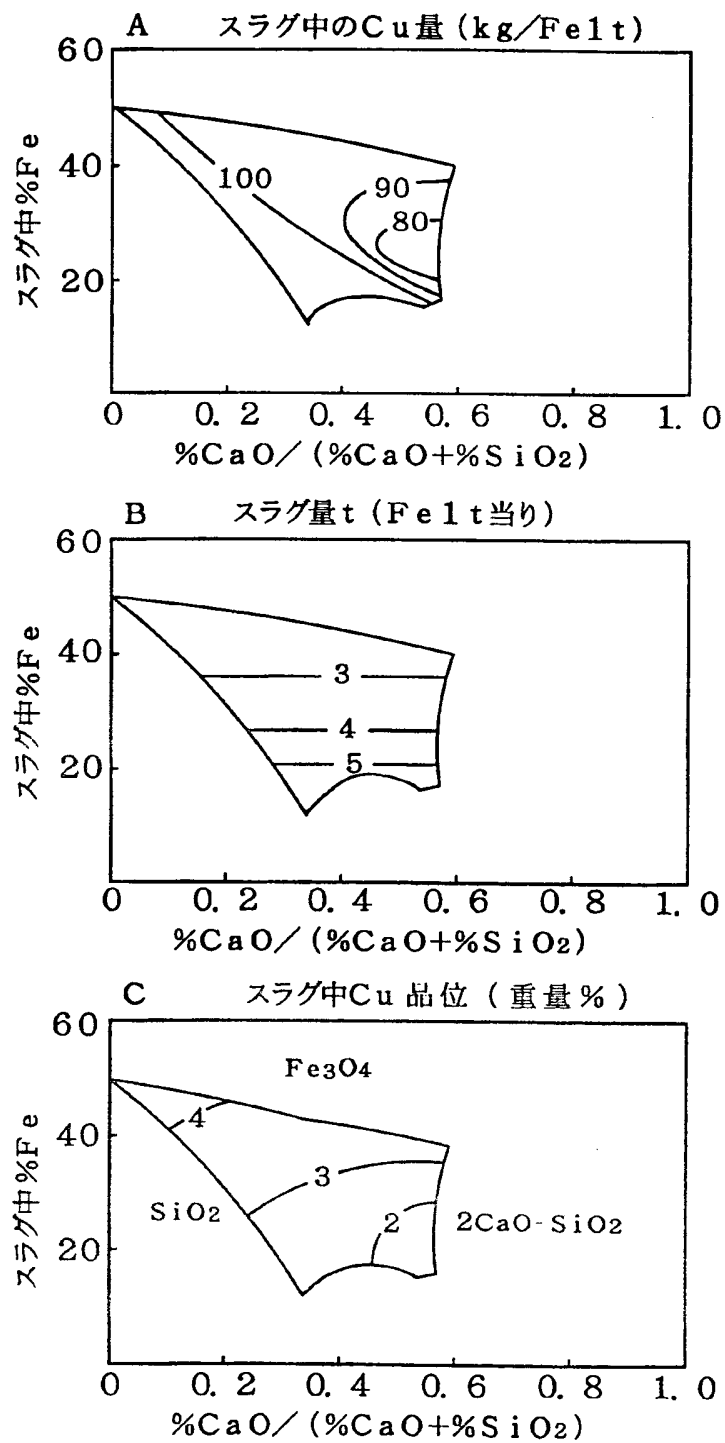
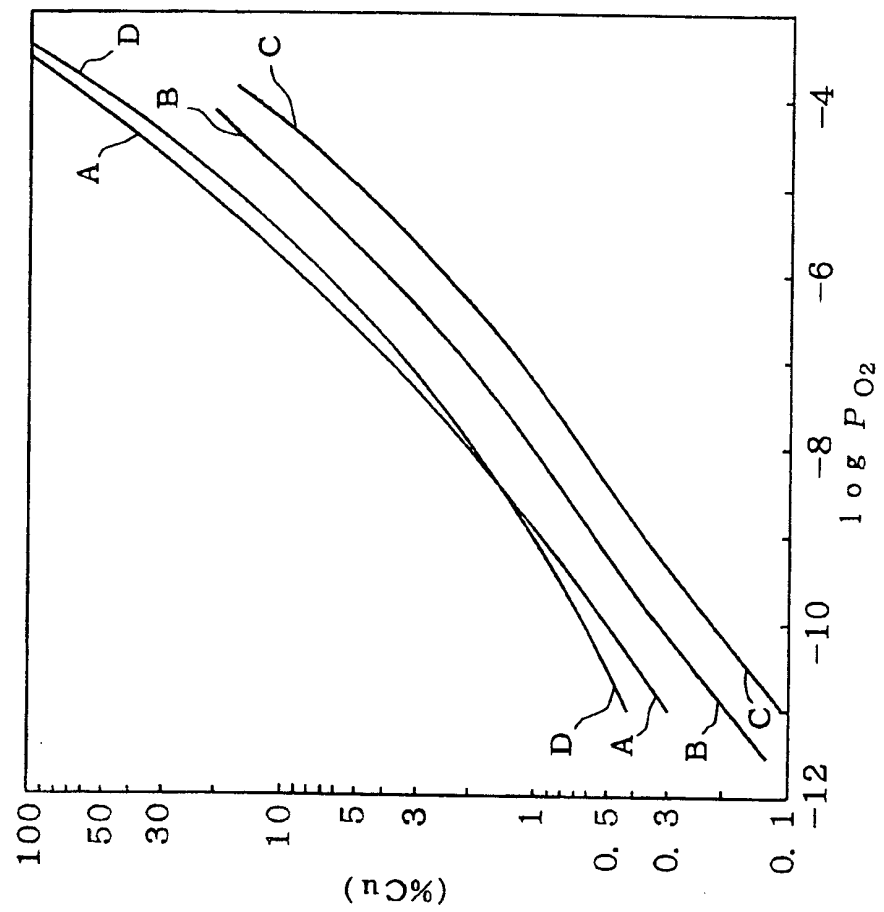


図 5



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/04350

A. CLASSIFICATION OF SUBJECT MATTER  
Int.Cl.<sup>6</sup> C22B15/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.<sup>6</sup> C22B15/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926-1996	Toroku Jitsuyo Shinan Koho	1994-1999
Kokai Jitsuyo Shinan Koho	1971-1999	Jitsuyo Shinan Toroku Koho	1994-1999

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 10-147821, A (MITSUBISHI MATERIALS CORPORATION), 02 June, 1998 (02.06.98), page 2, column 1 (Family: none)	1-10
A	JP, 5-214460, A (Inco Ltd.), 24 August, 1993 (24.08.93), page 2, column 1 (Family: none)	1-10
A	JP, 1-268824, A (SUMITOMO METAL MINING CO., LTD.), 26 October, 1989 (26.10.89), page 2, column 1 (Family: none)	1-10
A	JP, 1-268823, A (SUMITOMO METAL MINING CO., LTD.), 26 October, 1989 (26.10.89), page 2, column 1 (Family: none)	1-10

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

\* Special categories of cited documents:  
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 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
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 "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art  
 "&" document member of the same patent family

Date of the actual completion of the international search  
10 November, 1999 (10.11.99)Date of mailing of the international search report  
24 November, 1999 (24.11.99)Name and mailing address of the ISA/  
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

## 国際調査報告

国際出願番号 PCT/JP99/04350

A. 発明の属する分野の分類 (国際特許分類 (IPC))  
Int. Cl. C22B15/14

B. 調査を行った分野  
調査を行った最小限資料 (国際特許分類 (IPC))  
Int. Cl. C22B15/14

最小限資料以外の資料で調査を行った分野に含まれるもの  
 日本国実用新案 1926-1996  
 日本国公開実用新案公報 1971-1999  
 日本国登録実用新案公報 1994-1999  
 日本国実用新案登録公報 1994-1999

国際調査で利用した電子データベース (データベースの名称、調査に使用した用語)

## C. 関連すると認められる文献

引用文献の カテゴリ*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号
A	JP, 10-147821, A (三菱マテリアル株式会社), 2. 6月, 1998 (02. 06. 98), 第2頁, 第1欄 (ファミリーなし)	1-10
A	JP, 5-214460, A (インコ, リミテッド), 24. 8月, 1993 (24. 08. 93), 第2頁, 第1欄 (ファミリーなし)	1-10
A	JP, 1-268824, A (住友金属鉱山株式会社), 26. 10月, 1989 (26. 10. 89), 第2頁, 第1欄 (ファミリーなし)	1-10
A	JP, 1-268823, A (住友金属鉱山株式会社), 26. 10月, 1989 (26. 10. 89), 第2頁, 第1欄 (ファミリーなし)	1-10

☐ C欄の続きにも文献が列挙されている。

☐ パテントファミリーに関する別紙を参照。

## \* 引用文献のカテゴリ

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 「&」同一パテントファミリー文献

国際調査を完了した日 10. 11. 99

国際調査報告の発送日 24.11.99

国際調査機関の名称及びあて先  
 日本国特許庁 (ISA/JP)  
 郵便番号100-8915  
 東京都千代田区霞が関三丁目4番3号

特許庁審査官 (権限のある職員)  
 小柳 健 悟  
 電話番号 03-3581-1101 内線 3435

# PATENT ABSTRACTS OF JAPAN

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(51)Int.Cl.

C22B 15/14

(21)Application number : 10-229803

(71)Applicant : SUMITOMO METAL MINING CO LTD  
MITSUBISHI MATERIALS CORP

(22)Date of filing : 14.08.1998

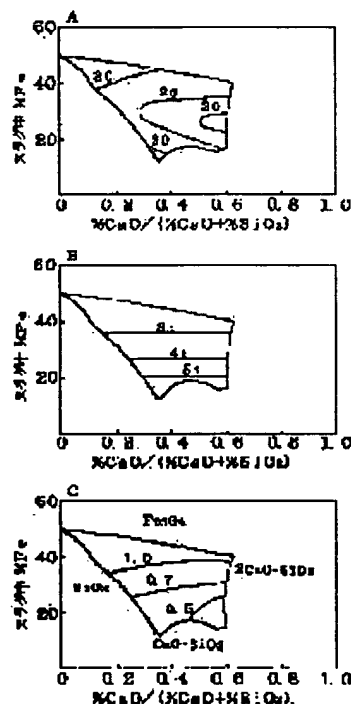
(72)Inventor : YAZAWA AKIRA  
TAKEDA YOICHI  
HASEGAWA NOZOMI  
MORI YOSHIKI

## (54) METHOD FOR SMELTING COPPER SULFIDE CONCENTRATE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide the smelting method of copper sulfide concentrate, in which in a process for obtaining white copper or blister copper by continuously oxidizing the copper sulfide concentrate or matte, a magnetite trouble is not developed and to apply this method to the treatment of the copper sulfide concentrate and the matte containing SiO<sub>2</sub>, so that the loss of copper into slag is little and furthermore, the copper content in the slag with a flotation can be recovered and the removing performance of AS, Sb and Pb into the slag is high and the wear loss of brick is little.

SOLUTION: In the method, in which the copper sulfide concentrate is oxidized and smelted and most of Fe in the copper sulfide concentrate is removed into the slag and also, a part or most of S is removed as SO<sub>2</sub> and the copper in the copper sulfide concentrate is obtd. as the white copper, the matte near the white copper or the blister copper, SiO<sub>2</sub> source and CaO source are added as solvent to the copper sulfide concentrate and the oxidizing and smelting is executed so as to produce the slag having 0.3-0.6 CaO/(SiO<sub>2</sub>+CaO) wt. ratio and 0.2-0.5 Fe/(FeOx+SiO<sub>2</sub>+CaO) wt. ratio and the white copper, the matte near the white copper or the blister copper.



## LEGAL STATUS

[Date of request for examination]

04.09.2000

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

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[Claim(s)]

[Claim 1] While carrying out oxidization refining of the copper sulfide mineral concentrate and removing the great portion of Fe in this copper sulfide mineral concentrate to a slag It is SO<sub>2</sub> in the great portion of the great portion of [ a part or ]. In the method of removing by carrying out and obtaining the copper in a copper sulfide mineral concentrate as the mat near a white regulus or a white regulus, or crude copper It is SiO<sub>2</sub> as a solvent to the aforementioned copper sulfide mineral concentrate. A source and the source of CaO are added. the weight ratio of CaO/(SiO<sub>2</sub>+CaO) by 0.3-0.6 And the refining method of the copper sulfide mineral concentrate characterized by carrying out oxidization refining so that the slag whose weight ratios of Fe/(FeOx+SiO<sub>2</sub>+CaO) are 0.2-0.5, and the mat or crude copper near a white regulus or a white regulus may be generated.

[Claim 2] The refining method of the copper sulfide mineral concentrate according to claim 1 characterized by repeating the collected copper content which ground and carried out flotation at an oxidization refining process after carrying out annealing solidification of the generated slag.

[Claim 3] SiO<sub>2</sub> in a copper sulfide mineral concentrate The refining method of a copper sulfide mineral concentrate according to claim 1 that a content is characterized by being 1.7 % of the weight or more to Fe which it is going to remove to a slag.

[Claim 4] The refining method of the copper sulfide mineral concentrate according to claim 1 characterized by controlling the temperature of the generated slag at 1300 degrees C or less.

[Claim 5] Oxidization refining of the copper sulfide mineral concentrate is carried out, Fe in this copper sulfide mineral concentrate reaches in part, and they are a slag and SO<sub>2</sub> in a part of S. It removes. obtained FeS and Cu<sub>2</sub>S the mat which is mixture -- further -- oxidization refining -- carrying out -- Fe and S -- a slag and SO<sub>2</sub> In the method of removing and obtaining crude copper \*\*\*\*\* -- It is SiO<sub>2</sub> to the aforementioned mat. A source and the source of CaO are added. the weight ratio of CaO/(SiO<sub>2</sub>+CaO) by 0.3-0.6 And the refining method of the copper sulfide mineral concentrate characterized by carrying out oxidization refining so that the slag whose weight ratios of Fe/(FeOx+SiO<sub>2</sub>+CaO) are 0.2-0.5, and crude copper may be generated.

[Claim 6] The refining method of the copper sulfide mineral concentrate according to claim 5 characterized by repeating the collected copper content which ground and carried out flotation at the oxidization refining process of a mat after carrying out annealing solidification of the generated slag.

[Claim 7] The refining method of the copper sulfide mineral concentrate according to claim 5 characterized by repeating the generated slag at the oxidization refining process of a mat with a melting state.

[Claim 8] The refining method of the copper sulfide mineral concentrate according to claim 5 characterized by repeating at the oxidization refining process of a mat after carrying out cooling solidification of the generated slag.

[Claim 9] SiO<sub>2</sub> in a mat The refining method of the copper sulfide mineral concentrate according to claim 5 characterized by being 1.7 % of the weight or more to Fe which a content tends to remove in a slag.

[Claim 10] The refining method of the copper sulfide mineral concentrate according to claim 5 characterized by controlling the temperature of the generated slag at 1300 degrees C or less.

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**DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] Especially this invention relates to the refinement method of carrying out oxidization refining of the mat obtained from the copper sulfide mineral concentrate or the copper sulfide mineral concentrate about a copper pyrometallurgy method, and obtaining a white regulus or crude copper.

[0002]

[Description of the Prior Art] While copper melting refinement carrying out oxidization fusion of the copper sulfide mineral concentrate, and oxidizing and removing a part of Fe in an ore as a slag conventionally a part of S -- SO<sub>2</sub> \*\* -- the mat refining process which carries out and condenses Cu as a mat which is the mixture of FeS and Cu<sub>2</sub> S -- subsequently like \*\*\*\*\* which oxidizes the obtained mat further, removes Fe as a slag, oxidizes further the white regulus manufacturing process which obtains the white regulus (Cu<sub>2</sub> S) which hardly contains Fe, and this white regulus, and obtains crude copper -- from -- it becomes Generally as a mat refining furnace, self-\*\*\*\* is used, and it is usually performed by the converter like a white regulus manufacturing process and \*\*\*\*\*.

[0003] Usually, in a copper sulfide mineral concentrate, it is SiO<sub>2</sub> as a part for a rock. Since it is contained, an iron silicate slag is used at a mat refining process. Also with a converter, usually, silicic acid ore is added as a solvent and an iron silicate slag is formed.

[0004] At a mat refining furnace, the copper grace in a mat (mat grade; MG) usually manufactures 70 or less % of the weight of a mat, and introduces this into a converter. a converter -- a batch type -- it is -- above -- a white regulus -- subsequently it considers as crude copper It is desirable to raise MG of a mat refining furnace and to lower the load of a batch-type converter, when raising the productivity of an entire plant. If it can oxidize to a white regulus at a mat refining furnace, the white regulus manufacturing process in a converter will become unnecessary. Furthermore, if it can oxidize to crude copper, the converter process itself will become unnecessary. However, when it was going to raise the degree of oxidization of a mat refining furnace, there were the following problems resulting from an iron silicate slag.

[0005] (1) Magnetite trouble : with an iron silicate slag, the solubility of trivalent Fe is a low. For this reason, the so-called magnetite trouble is caused, such as a solid-state magnetite depositing and depositing to a blast furnace bottom. In order to avoid this, when making MG high, refining temperature must be raised to 1300 degrees C or more. However, this promotes the injury on a furnace body. Moreover, if it oxidizes in copper [ some ] and copper grace in a slag is made high, although a magnetite trouble will be avoided and crude copper will be obtained also with an iron silicate slag, the copper grace in the slag at this time is 25% or more need, and the yield of crude copper becomes remarkably low.

[0006] (2) Copper oxidizing melting : the solubility as an oxide of the copper to the inside of an iron silicate slag rises remarkably with elevation of MG.

[0007] (3) Concentration of an impurity : under coexistence of an iron silicate slag, a mat, or crude copper, these impurities condense [ the solubility to the iron silicate slag of oxides, such as As and Sb ] in a mat or crude copper to a low sake. When an iron silicate slag and crude copper lived together, especially, it was remarkable and was referred to as one of the reasons which cannot obtain direct crude copper from the high copper sulfide mineral concentrate of these impurities under iron silicate slag coexistence by the extent.

[0008] From these points, operation is usually performed at the mat refining furnace using an iron silicate slag by making about 65 - 70% of MGs into an upper limit.

[0009] Moreover, in the process which oxidizes a mat from the same problem even to the low crude copper of S grace, under iron silicate slag coexistence, continuation-ization was made impossible and processing of the batch type using the converter has usually been performed. that from which this obtained crude copper under three-phase-circuit coexistence of slag-white regulus-crude copper although there was also a report (JP,58-224128,A) which has obtained crude copper from the mat continuously under iron silicate slag coexistence -- it is -- S grace in the crude copper at this time -- 1.5% -- high -- not becoming -- it does not obtain but the operation load of the refining furnace which is a back process is increased remarkably

[0010] Avoiding this problem, one of invention-in-this-application persons has proposed the method of manufacturing a white regulus at a mat refining furnace, by JP,5-15769,B. This adds lime as a solvent and removes the iron in a copper sulfide mineral concentrate as a calcium ferrite slag. By using a calcium ferrite slag, the deposit of a magnetite could be prevented and had the advantage that the elimination factor to the slag of impurities, such as As and Sb, was higher than an iron silicate slag. However,



there were the following problems.

[0011] (1) In a copper sulfide mineral concentrate, it is usually  $\text{SiO}_2$  of a some. It is contained. For this reason, the copper sulfide mineral concentrate processed in order to make as pure a calcium ferrite slag as possible generate is  $\text{SiO}_2$ . It is restricted to the low thing (3% or less) of grace.

[0012] (2) Above low  $\text{SiO}_2$  Even if it is a copper sulfide mineral concentrate, it is  $\text{SiO}_2$  little in a calcium ferrite slag. When it existed, the viscosity of a slag was worsened, or foaming was caused and stable \*\*\*\* was difficult. For this reason, when using a calcium ferrite slag, it is  $\text{SiO}_2$  in a slag. Grace is  $\text{SiO}_2$  in a copper sulfide mineral concentrate practically, when it is going to obtain a white regulus from the standard copper sulfide mineral concentrate which had to control to 1% or less (it is about 1.7% or less at a weight to Fe in a slag), and made the KARUKO pyrite the subject by this method. Grace was limited to 0.4% or less.

[0013] (3) Since the solubility of Pb to a calcium ferrite slag is low, Pb is hard to be distributed into this slag, and condenses to a white regulus.

[0014] (4) There are many amounts of dissolutions as an oxide of the copper to a calcium ferrite slag, and the recovery by sifting is low.

[0015] When oxidizing further and making a mat into a white regulus and crude copper at a convertor process on the other hand, in order to avoid the problem resulting from an iron silicate slag, a process is used as a batch, and once interrupt blowing for the state where a white regulus and a slag live together, a furnace is made to \*\*\*\*, a slag is discharged, it leaves in convertor of only a white regulus, and oxidization to crude copper is performed. This method includes the various disadvantageous profits resulting from a batch method, and makes convertor operation complicated.

[0016] By the Mitsubishi continuation copper-metallurgy method, the deposit of a magnetite is avoided by using a calcium ferrite slag at a convertor (C furnace) process, and crude copper is continuously manufactured from the about [ MG65% ] mat. However, there were the following problems resulting from a calcium ferrite slag.

[0017] (1) The copper grace in a slag changes continuously to oxygen tension, and the copper grace in a slag becomes high, so that S grace in crude copper is lowered. Practically, it is not efficient from the point of copper yield for Cu in a slag to become 13 - 15% at about 0.5 - 1%, and to make S in crude copper into S grace not more than this.

[0018] (2) For the copper content in a calcium ferrite slag, the recovery of the copper by sifting even if it dissolves chemically and cools slowly mainly with an oxide is a low.

[0019] (3) As mentioned above,  $\text{SiO}_2$  in a calcium ferrite slag If it becomes about 1 - 3%, viscosity will increase remarkably and foaming (foaming) will be started. For this reason, the mat which the iron silicate slag mixed was difficult to use it as a raw material.  $\text{SiO}_2$  which can permit mixing into a mat if Fe grace in a mat is made into 10% To the mat, it is 0.2% or less and needed to be cautious of especially mixing prevention of the slag to the mat produced from a mat refining process.

[0020] (4) For a low reason, Pb is hard to be distributed into a slag and the solubility of Pb condenses to crude copper. For this reason, manufacture of the anode which can be electrolyzed by the conventional method from a high Pb raw material was difficult.

[0021] (5) When the same temperature compares, since the permeability to brick is large, the corrosion nature of convertor brick is larger than a silicate slag.

[0022]

[Problem(s) to be Solved by the Invention] When oxidizing a copper sulfide mineral concentrate or a mat continuously and obtaining a white regulus or crude copper, the purpose of this invention (1) There is no magnetite trouble at the usual copper refining temperature of 1300 degrees C or less. (2)  $\text{SiO}_2$  Can apply also to processing of the copper sulfide mineral concentrate and mat to contain, there is little loss of the copper to (3) slags, and recovery of the copper content in a slag is possible by (4) flotation. (5) The removal ability to the slag of As, Sb, and Pb is high, and is to offer the refining method of a copper sulfide mineral concentrate with little \*\*\*\* of (6) bricks.

[0023]

[Means for Solving the Problem] The method of this invention is  $\text{SiO}_2$  as a solvent to a copper sulfide mineral concentrate. It is characterized by carrying out oxidization refining so that the mat near the slag and white regulus whose weight ratios of  $\text{Fe}/(\text{FeOx}+\text{SiO}_2+\text{CaO})$  a source and the source of CaO are added, and the weight ratios of  $\text{CaO}/(\text{SiO}_2+\text{CaO})$  are 0.3-0.6, and are 0.2-0.5, a white regulus, or crude copper may be generated.

[0024] Moreover, it is  $\text{SiO}_2$  to the mat obtained by carrying out refining of the copper sulfide mineral concentrate. It is characterized by carrying out oxidization refining so that the slag and crude copper whose weight ratios of  $\text{Fe}/(\text{FeOx}+\text{SiO}_2+\text{CaO})$  a source and the source of CaO are added, and the weight ratios of  $\text{CaO}/(\text{SiO}_2+\text{CaO})$  are 0.3-0.6, and are 0.2-0.5 may be generated.

[0025] The iron calcium silicate slag which uses the feature of the slag in the high oxygen tension conditions which manufacture a white regulus or crude copper by the iron silicate slag conventionally used by copper refinement, the calcium ferrite slag used by the Mitsubishi method, and this invention is compared, and is shown in Table 1.

[0026]

[Table 1]

	鉄シリケート スラグ	カルシウムフェラ イトスラグ	鉄カルシウムシリ ケートスラグ
粘性が低い	×	○	○
マット、粗銅の 懸垂が少ない	×	○	○
銅の酸化溶解が 少ない	×	×	○
銅の硫化溶解が 少ない	○	×	×
Pbの溶解度が 高い	○	×	○
As, Sb溶解度	×	○	○
Mg 矽溶解度	×	○	○
煉瓦の熔損が 少ない	○	×	○

[0027] Adding some CaO to an iron silicate slag, and improving viscosity conventionally, has been performed. However, at the mat refining process, if CaO grace becomes high, since the solubility as a copper sulfide will increase and also the amount of slags will also increase, it has been thought that it is disadvantageous. However, under the conditions which coexist with the white regulus from which the sulfurization dissolution does not pose a problem, or crude copper With the iron calcium silicate slag used by this invention, to copper oxidizing melting increasing remarkably in an iron silicate slag or a calcium ferrite slag Since there is little copper oxidizing melting and it ends, if the amount of losses of the copper by amount of slags  $\times$  copper grace = oxidizing melting estimates It found out becoming less than a conventional method (the mat refining method, white regulus refining, and the direct copper-metallurgy method of high MG using an iron silicate slag or a calcium ferrite slag), and resulted in this invention.

[0028] Drawing 1 is the graph which showed the copper grace (C) in the copper quantity in the 1300-degree C slag in the case of oxidizing a copper sulfide mineral concentrate and obtaining the mat of MG75 (A), the amount of slags (B) to generate, and a slag to the weight ratio (horizontal axis) of CaO/in a slag ( $\text{SiO}_2 + \text{CaO}$ ), and Fe% (vertical axis). The saturation line of each solid phase is shown in each drawing, and the weight ratios of CaO/( $\text{SiO}_2 + \text{CaO}$ ) are 2 CaO-SiO<sub>2</sub> or more in 0.6. It deposits. Moreover, if Fe grace is too high, a magnetite deposits. The left end of drawing is equivalent to the conventional iron silicate slag (CaO=0%).

[0029] It is in the inclination for copper grace to become low, so that the iron grace in a slag becomes low, and copper grace becomes low, so that the weight ratio of CaO/( $\text{SiO}_2 + \text{CaO}$ ) is large. The amount of slags decreases, so that the iron grace in a slag is high, since the amount of slags to generate is decided by iron grace in a slag and \*\*\*\* which should be removed is decided with a raw material. As the copper quantity (the amount of losses) which shifts to a slag is decided by copper grace in an amount of slags  $\times$  slag and was shown in the best stage, 0.5 to 0.6 and the weight ratio of Fe/( $\text{FeOx} + \text{SiO}_2 + \text{CaO}$ ) have [ the weight ratio of CaO/( $\text{SiO}_2 + \text{CaO}$ ) ] the minimal value near composition of 0.2-0.5. Namely, what is necessary is just to choose the slag of composition of this neighborhood from the point of making loss of the copper to the inside of a slag into the minimum.

[0030] On the other hand, drawing 2 is the graph which showed the activity coefficient of As in a slag to slag composition. The weight ratio of CaO/( $\text{SiO}_2 + \text{CaO}$ ) is shown in the horizontal axis, and the activity coefficient ( $\gamma_{\text{AsO}1.5}$ ) of As is shown in the vertical axis. The iron silicate slag of the former [ left end / of drawing ] and a right end are equivalent to a calcium ferrite slag, and the iron calcium silicate slag used by this invention is located in both middle. An activity coefficient shows that the element is easy to be removed in a slag, so that a value is small.

[0031] From drawing 2, when the weight ratio of CaO/( $\text{SiO}_2 + \text{CaO}$ ) is made or more into 0.3, a bird clapper understands the removal ability of As more highly than an iron silicate slag. In addition, behavior with the same said of Sb belonging to the same V group as As is shown.

[0032] On the other hand, as shown in drawing 3, Pb shows reverse behavior, and the activity coefficient ( $\gamma_{\text{PbO}}$ ) of Pb serves as a remarkable big value by the calcium ferrite slag, and shows forge-fire small \*\*\*\*\* with the small weight ratio of CaO/( $\text{SiO}_2 + \text{CaO}$ ). Although the removal ability of Pb is a little inferior in the weight ratio of CaO/( $\text{SiO}_2 + \text{CaO}$ ) by 0.3-0.6 compared with an iron silicate slag, compared with the calcium ferrite slag, it has quite big removal ability.

[0033] As mentioned above, a bird clapper is known that it is easy to remove in a slag about both As Sb and Pb by setting the weight ratio of CaO/( $\text{SiO}_2 + \text{CaO}$ ) to 0.3-0.6.

[0034] Drawing 4 shows the same relation as drawing 1 about the case where the crude copper of about 1 - 1.5% of S grace is obtained under white regulus coexistence. The left end of drawing is equivalent to an iron silicate slag (CaO=0%), and a right end is equivalent to a calcium ferrite slag (2 = 0% of SiO(s)). From drawing of the best stage, the copper amount of losses is 2

CaO-SiO<sub>2</sub>. It turns out that the minimum is taken in the place near a saturation line. Although the copper amount of losses also has comparatively few calcium ferrite slags, it is little SiO<sub>2</sub>. When carried in, it is 2 CaO-SiO<sub>2</sub>. It becomes saturation and the problem of foaming of a slag is produced.

[0035] About distribution of an impurity, a calcium ferrite slag cannot absorb Pb easily, to there being a fault of being hard to absorb As and Sb, is setting the weight ratio of CaO/(SiO<sub>2</sub>+CaO) to 0.3-0.6, and becomes easy to be in the same inclination as mat refining, and to remove both As Sb and P in a slag in an iron silicate slag.

[0036] As mentioned above, it turns out that there is the optimal composition whose weight ratio of CaO/(SiO<sub>2</sub>+CaO) the weight ratio of 0.3 to 0.6 and Fe/(FeOx+SiO<sub>2</sub>+CaO) carries out copper loss to the range of 0.2-0.5 at the minimum, and tends to remove both Pb As and Sb.

[0037] Drawing 5 is what showed the copper grace in the slag to oxygen tension, and the behavior in the case of obtaining the low crude copper of S grace in the field where the degree of oxidization is still higher is shown from the case where it is shown in drawing 4. The inside of drawing and Curve A show the iron calcium silicate slag which an iron silicate slag and Curve D use by the calcium ferrite slag, and Curves B and C use by this invention. In an iron silicate slag and a calcium ferrite slag, the copper in a slag changes continuously to 100% according to elevation of oxygen tension. Since it becomes copper-oxide saturation by about 20% of copper grace with an iron calcium silicate slag to it, the copper grace in a slag does not go up more than this grace. That is, if crude copper is made from this condition, 0.01% or less of crude copper (crude copper of copper-oxide saturation) will be obtained [ the copper grace in a slag ] for S grace at about 20%. If the crude copper of the degree of oxidization of the same grade is made from an iron silicate slag or a calcium ferrite slag, the copper grace in a slag will become remarkably high, and will not serve as practical use from the point of yield.

[0038] About the corrosion of brick, osmosis in the brick of a slag component is considered to do big influence. Usually, when a slag component permeates into the magnesite chrome brick used by copper refinement, it is known that the iron oxide in a slag will be absorbed by the spinel containing a periclase (MgO) or Cr<sub>2</sub>O<sub>3</sub>. SiO<sub>2</sub> When it permeates into brick in the case of the included slag, and an iron oxide dissolves in a periclase (MgO) or a spinel, it is SiO<sub>2</sub> in a slag. Concentration becomes high. Consequently, the viscosity of a slag goes up and it is thought that the slag osmosis beyond it is suppressed.

[0039]

[Example] [Example 1] Melting mat 40g and 60g of molten slags shown in Table 2 are prepared in the crucible made from a magnesia held at 1300 degrees C. The copper sulfide mineral concentrate of the composition shown in Table 2 the same during a melting bath, and SiO<sub>2</sub> (SiO<sub>2</sub> pure 95% or more per part) and CaO (CaO pure 98% or more per part) were blown without immersing a lance pipe with 95%O<sub>2</sub>-5% N<sub>2</sub> (capacity %) using a lance pipe.

[0040]

[Table 2]

(重量%)

	Cu	Fe	S	SiO <sub>2</sub>	CaO
熔融マット	74.8	2.0	20.5	—	—
熔融スラグ	2.4	35.1	—	22.9	16.2
硫化銅精鉱	31.4	24.0	30.2	6.9	—

[0041] The lance pipe used for the entrainment is a product made from an alumina, and blew 20gSiO<sub>2</sub> for copper sulfide mineral concentrate and 1.94g/for /, and 2.20gCaO for /with 95%O<sub>2</sub>-5%N<sub>2</sub> (capacity %) gas for 4.5l/.

[0042] After continuing an entrainment for 50 minutes on condition that the above and standing it still for 10 minutes, cooling solidification is carried out, a mat and the weight row of a slag are asked for analysis grace, each amount of components is deducted from grace in the mat inserted in first and the amount row of a slag, and the result which calculated the grace in the amount of mats generated by the reaction and the amount row of slags is shown in Table 3.

[0043]

[Table 3]

(重量%)

	産出重量 (g)	Cu	Fe	S	SiO <sub>2</sub>	CaO
生成マット	375	76.2	1.0	20.1	—	—
生成スラグ	641	1.9	35.0	—	23.8	16.0

[0044]

[Example 2] 30g of melting crude copper and 80g of molten slags of the composition shown in Table 4 are prepared in the crucible made from a magnesia held at 1300 degrees C. The copper sulfide mineral concentrate of the composition shown in Table 4 the same during a melting bath, and SiO<sub>2</sub> (SiO<sub>2</sub> pure 95% or more per part) and CaO (CaO pure 98% or more per part) were blown without immersing a lance pipe with 95%O<sub>2</sub>-5% N<sub>2</sub> (capacity %) using a lance pipe.

[0045]

[Table 4]

(重量%)

	Cu	Fe	S	SiO <sub>2</sub>	CaO
溶融粗銅	97.5	—	1.2	—	—
溶融スラグ	3.8	31.0	—	26.1	18.2
硫化銅精鉱	31.4	24.0	30.2	6.9	—

[0046] The lance pipe used for the entrainment is a product made from an alumina, and blew 20gSiO<sub>2</sub> for copper sulfide mineral concentrate and 3.02g/for /, and 2.88gCaO for /with 95%O<sub>2</sub>-5%N<sub>2</sub> (capacity %) gas for 5.8l./.

[0047] After continuing an entrainment for 50 minutes on condition that the above and standing it still for 10 minutes, cooling solidification is carried out, crude copper and the weight row of a slag are asked for analysis grace, each amount of components is deducted from grace in the crude copper and the amount row of a slag which were inserted in first, and the result which calculated the grace in the amount of crude copper generated by the reaction and the amount row of slags is shown in Table 5.

[0048]

[Table 5]

(重量%)

	産出重量 (g)	Cu	Fe	S	SiO <sub>2</sub>	CaO
生成粗銅	273	98.1	—	0.99	—	—
生成スラグ	764	4.2	29.8	—	26.3	17.9

[0049]

[Example 3] 60g of melting crude copper and 40g of molten slags of the composition shown in Table 6 were prepared in the crucible made from a magnesia held at 1300 degrees C, and the mat of the composition shown in Table 6 the same during a melting bath, and SiO<sub>2</sub> (SiO<sub>2</sub> pure 95% or more per part) and CaO (CaO pure 98% or more per part) were blown with 95%O<sub>2</sub>-5% N<sub>2</sub> (capacity %), without immersing a lance pipe.

[0050]

[Table 6]

(重量%)

	Cu	Fe	S	SiO <sub>2</sub>	CaO
溶融粗銅	97.5	—	1.2	—	—
溶融スラグ	18.4	25.3	—	22.1	13.5
マット	65.3	9.7	21.4	—	—

[0051] The lance pipe used for the entrainment is a product made from an alumina, and is 20gSiO<sub>2</sub> for copper sulfide mineral concentrate and 1.78g/for /. 1.14gCaO for /was blown with 95%O<sub>2</sub>-5%N<sub>2</sub> (capacity %) gas for 4.0l./.

[0052] After continuing an entrainment for 50 minutes on condition that the above and standing it still for 10 minutes, cooling solidification is carried out, crude copper and the weight row of a slag are asked for analysis grace, each amount of components is deducted from grace in the crude copper and the amount row of a slag which were inserted in first, and the result which calculated the grace in the amount of crude copper generated by the reaction and the amount row of slags is shown in Table 7.

[0053]

[Table 7]

(重量%)

	産出重量 (g)	Cu	Fe	S	SiO <sub>2</sub>	CaO
生成粗銅	558	98.8	—	0.05	—	—
生成スラグ	382	20.6	24.9	—	20.8	14.0

[0054] In the examination of these examples 1-3, the dust incidence rate was 4 - 7% of the weight of a range. In the meantime, there was no trouble by generating of a magnetite.

[0055]

[Example 4] The slag generated in the example 3 was pulverized with the ball mill until the 200-mesh undershirt became 95%, this slag 200g was made into the slurry 65% of the weight with water, and the flotation test was carried out with the flotation machine for an examination. Under the present circumstances, DM-2000 of marketing, MCB-4, and 0.006g of 0.01g of 0.03g of xanthates were respectively added as 0.02g of pine oils, and a flotation reagent as a frothing agent.

[0056] A test result is shown in Table 8. It was checked that 80% or more of copper is recoverable with flotation.

[0057]

[Table 8]

原鉱	精鉱		尾鉱	
Cu%	Cu%	分布	Cu%	分布
20.8	38	81	1.5	19

[0058]

[Example 5] The bore of 1.5m of a reactor, a height of 3.5m, the bore of 1.5m of the settler section, The mineral concentrate, powder silica, and powder lime (what ground all to 200 micrometers or less) of composition which were shown in Table 9 are prepared by the predetermined ratio using small self-\*\*\*\* with a length of 5.2m. It blew in into the reactor with oxygen-enrichment air of 50% of oxygen from the mineral concentrate burner in which the dry thing (henceforth \*\*\*\*) was prepared by the reactor ceiling, and the slag and the mat were obtained. The fuel oil burner is included in the mineral concentrate burner, and the amount of fuel oils was adjusted so that the heat balance of a reactor might be maintained. Operation was performed for four days. The obtained result is shown in Table 9. Table 9 shows that the high-definition mat of MG 76 [ about ] was obtained stably.

[0059]

[Table 9]

(重量%)

		物量 (kg/h)	Cu	Fe	S	SiO <sub>2</sub>	CaO
処理	硫化銅精鉱	1040	31.4	25.1	30.2	6.9	—
	珪石	104	—	2	—	95	
	石灰石	208	—	—	—	—	53
産出	熔融マット	382	76.8	1.0	20.1	—	—
	熔融スラグ	700	2.5	35.0	—	24.2	16.1

精鉱バーナー送風空気量 580 Nm<sup>3</sup> / h、酸素濃度 50%、

重油量 53 リットル / h、

生成スラグ平均温度 1258℃、生成マット平均温度 1146℃

[0060]

[The example 1 of comparison] Melting mat 30g of the composition shown in Table 10 and 40g of molten slags were prepared in the crucible made from a magnesia held at 1300 degrees C, and the copper sulfide mineral concentrate of the composition shown in Table 10 the same during a melting bath and SiO<sub>2</sub> (SiO<sub>2</sub> pure 97% or more per part) were blown with 95%O<sub>2</sub>-5% N<sub>2</sub> (capacity %), without immersing a lance pipe.

[0061]

[Table 10]

(重量%)

	Cu	Fe	S	SiO <sub>2</sub>	CaO
熔融マット	76.3	2.8	20.8	—	—
熔融スラグ	5.0	42.0	—	30.0	—
硫化銅精鉱	30.3	29.1	33.5	1.8	—

[0062] The lance pipe used for the entrainment is a product made from an alumina, and is 37.5gSiO<sub>2</sub> for copper sulfide mineral concentrate and 7.6g/for /. It blew in with 95%O<sub>2</sub>-5%N<sub>2</sub> (capacity %) gas for 9.2l/.

[0063] After [ of a test start ] 5 minutes, by formation of the high-melting point matter which the generation magnetite mixed with the mat, the entrainment to the inside of the melt of a feed became impossible, and further, for these matter, lock out of a lance

pipe took place and it became uncontinuable [ an experiment ].

[0064]

[The example 2 of comparison] 60g of melting crude copper and 40g of molten slags of the composition shown in Table 11 were prepared in the crucible made from a magnesia held at 1300 degrees C, and the mat and CaO (CaO pure 98% or more per part) of the composition shown in Table 11 the same during a melting bath were blown with 95%O<sub>2</sub>-5% N<sub>2</sub> (capacity %), without immersing a lance pipe.

[0065]

[Table 11]

(重量%)

	Cu	Fe	S	SiO <sub>2</sub>	CaO
溶融粗銅	97.5	—	1.2	—	—
溶融スラグ	16.4	47.6	—	—	17.6
マット	64.0	9.5	21.0	2.0	—

[0066] The lance pipe used for the entrainment is a product made from an alumina, and blew 20g mat for /, and 0.73gCaO for /with 95%O<sub>2</sub>-5%N<sub>2</sub> (capacity %) gas for 0.20l./.

[0067] The boiling phenomenon of a slag happened after [ of a test start ] 30 minutes, the great portion of \*\*\*\* in a crucible boiled over out of the crucible, and it became uncontinuable [ an experiment ].

[0068]

[The example 3 of comparison] 60g of melting crude copper and 40g of molten slags of the composition shown in Table 12 were prepared in the crucible made from a magnesia held at 1300 degrees C, and the mat and CaO (CaO pure 98% or more per part) of the composition shown in Table 12 the same during a melting bath were blown with 95%O<sub>2</sub>-5% N<sub>2</sub> (capacity %), without immersing a lance pipe.

[0069]

[Table 12]

(重量%)

	Cu	Fe	S	SiO <sub>2</sub>	CaO
溶融粗銅	97.5	—	1.2	—	—
溶融スラグ	16.4	47.6	—	—	15.7
マット	65.3	9.7	21.4	—	—

[0070] The lance pipe used for the entrainment is a product made from an alumina, and blew 20g mat for /, and 0.7gCaO for /with 95%O<sub>2</sub>-5%N<sub>2</sub> (capacity %) gas for 4.2l./.

[0071] After continuing an entrainment for 50 minutes on condition that the above and standing it still for 10 minutes, cooling solidification is carried out, crude copper and the weight row of a slag are asked for analysis grace, each amount of components is deducted from grace in the crude copper and the amount row of a slag which were inserted in first, and the result which calculated the grace in the amount of crude copper generated by the reaction and the amount row of slags is shown in Table 13.

[0072] Although the crude copper of 0.06% of S grace was obtained, the copper grace in a slag was high and the yield of crude copper was about 80%.

[0073]

[Table 13]

(重量%)

	産出重量 (g)	Cu	Fe	S	SiO <sub>2</sub>	CaO
生成粗銅	534	98.3	—	0.06	—	—
生成スラグ	290	32.7	32.0	—	—	11.2

[0074]

[The example 4 of comparison] The calcium ferrite slag containing Cu16.4%, Fe47.6%, and CaO15.7% was pulverized with the ball mill until the 200-mesh undershirt became 95%, this slag 200g was made into the slurry 65% of the weight with water, and the flotation test was carried out with the flotation machine for an examination. Under the present circumstances, DM-2000 of marketing, MCB-4, and 0.006g of 0.01g of 0.03g of xanthates were respectively added as 0.02g of pine oils, and a flotation reagent as a frothing agent.

[0075] A test result is shown in Table 14. It was difficult to collect copper from a calcium ferrite slag with flotation.

[0076]

[Table 14]

原鉱	精鉱		尾鉱	
Cu%	Cu%	分布	Cu%	分布
16.4	21	54	10	46

[0077]

[Effect of the Invention] When oxidizing a copper sulfide mineral concentrate or a mat continuously and obtaining a white regulus or crude copper by the method of this invention, there is no magnetite trouble and it is SiO<sub>2</sub>. It is applicable also to processing of the copper sulfide mineral concentrate and mat to contain, and there is little loss of the copper to a slag, and recovery of the copper content in the slag by flotation is possible, the removal ability to the slag of As, Sb, and Pb is high, and refining of a copper sulfide mineral concentrate with little \*\*\*\* of

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[Translation done.]

**\*NOTICES\***

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**TECHNICAL FIELD**

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[The technical field to which invention belongs] Especially this invention relates to the refinement method of carrying out oxidization refining of the mat obtained from the copper sulfide mineral concentrate or the copper sulfide mineral concentrate about a copper pyrometallurgy method, and obtaining a white regulus or crude copper.

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[Translation done.]



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PRIOR ART

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[Description of the Prior Art] While copper melting refinement carrying out oxidization fusion of the copper sulfide mineral concentrate, and oxidizing and removing a part of Fe in an ore as a slag conventionally a part of S -- SO<sub>2</sub> \*\* -- like \*\*\*\*\* which carries out, subsequently oxidizes further the mat refining process which condenses Cu as a mat which is the mixture of FeS and Cu<sub>2</sub> S, and the obtained mat, removes Fe as a slag, oxidizes further the white regulus manufacturing process which obtains the white regulus (Cu<sub>2</sub> S) which hardly contains Fe, and this white regulus, and obtains crude copper -- from -- it becomes Generally as a mat refining furnace, self-\*\*\*\* is used, and it is usually performed by the converter like a white regulus manufacturing process and \*\*\*\*\*.

[0003] Usually, in a copper sulfide mineral concentrate, it is SiO<sub>2</sub> as a part for a rock. Since it is contained, an iron silicate slag is used at a mat refining process. Also with a converter, usually, silicic acid ore is added as a solvent and an iron silicate slag is formed.

[0004] At a mat refining furnace, the copper grade in a mat (mat grade; MG) usually manufactures 70 or less % of the weight of a mat, and introduces this into a converter. a converter -- a batch type -- it is -- above -- a white regulus -- subsequently it considers as crude copper. It is desirable to raise MG of a mat refining furnace and to lower the load of a batch-type converter, when raising the productivity of an entire plant. If it can oxidize to a white regulus at a mat refining furnace, the white regulus manufacturing process in a converter will become unnecessary. Furthermore, if it can oxidize to crude copper, the converter process itself will become unnecessary. However, when it was going to raise the degree of oxidization of a mat refining furnace, there were the following problems resulting from an iron silicate slag.

[0005] (1) Magnetite trouble : with an iron silicate slag, the solubility of trivalent Fe is a low. For this reason, the so-called magnetite trouble is caused, such as a solid-state magnetite depositing and depositing to a blast furnace bottom. In order to avoid this, when making MG high, refining temperature must be raised to 1300 degrees C or more. However, this promotes the injury on a furnace body. Moreover, if it oxidizes in copper [ some ] and copper grade in a slag is made high, although a magnetite trouble will be avoided and crude copper will be obtained also with an iron silicate slag, the copper grade in the slag at this time is 25% or more need, and the yield of crude copper becomes remarkably low.

[0006] (2) Copper oxidizing melting : the solubility as an oxide of the copper to the inside of an iron silicate slag rises remarkably with elevation of MG.

[0007] (3) Concentration of an impurity : under coexistence of an iron silicate slag, a mat, or crude copper, these impurities condense [ the solubility to the iron silicate slag of oxides, such as As and Sb ] in a mat or crude copper to a low sake. When an iron silicate slag and crude copper lived together, especially, it was remarkable and was referred to as one of the reasons which cannot obtain direct crude copper from the high copper sulfide mineral concentrate of these impurities under iron silicate slag coexistence by the extent.

[0008] From these points, operation is usually performed at the mat refining furnace using an iron silicate slag by making about 65 - 70% of MGs into an upper limit.

[0009] Moreover, in the process which oxidizes a mat from the same problem even to the low crude copper of S grade, under iron silicate slag coexistence, continuation-ization was made impossible and processing of the batch type using the converter has usually been performed. that from which this obtained crude copper under three-phase-circuit coexistence of slag-white regulus-crude copper although there was also a report (JP,58-224128,A) which has obtained crude copper from the mat continuously under iron silicate slag coexistence -- it is -- S grade in the crude copper at this time -- 1.5% -- high -- not becoming -- it does not obtain but the operation load of the refining furnace which is a back process is increased remarkably

[0010] Avoiding this problem, one of invention-in-this-application persons has proposed the method of manufacturing a white regulus at a mat refining furnace, by JP,5-15769,B. This adds lime as a solvent and removes the iron in a copper sulfide mineral concentrate as a calcium ferrite slag. By using a calcium ferrite slag, the deposit of a magnetite could be prevented and had the advantage that the elimination factor to the slag of impurities, such as As and Sb, was higher than an iron silicate slag. However, there were the following problems.

[0011] (1) In a copper sulfide mineral concentrate, it is usually SiO<sub>2</sub> of a some. It is contained. For this reason, the copper sulfide mineral concentrate processed in order to make as pure a calcium ferrite slag as possible generate is SiO<sub>2</sub>. It is restricted to the low thing (3% or less) of grade.

[0012] (2) Above low SiO<sub>2</sub> Even if it is a copper sulfide mineral concentrate, it is SiO<sub>2</sub> little in a calcium ferrite slag. When it existed, the viscosity of a slag was worsened, or foaming was caused and stable \*\*\*\* was difficult. For this reason, when using a

calcium ferrite slag, it is  $\text{SiO}_2$  in a slag. Grace is  $\text{SiO}_2$  in a copper sulfide mineral concentrate practically, when it is going to obtain a white regulus from the standard copper sulfide mineral concentrate which had to control to 1% or less (it is about 1.7% or less at a weight to Fe in a slag), and made the KARUKO pyrite the subject by this method. Grace was limited to 0.4% or less.

[0013] (3) Since the solubility of Pb to a calcium ferrite slag is low, Pb is hard to be distributed into this slag, and condenses to a white regulus.

[0014] (4) There are many amounts of dissolutions as an oxide of the copper to a calcium ferrite slag, and the recovery by sifting is low.

[0015] When oxidizing further and making a mat into a white regulus and crude copper at a convertor process on the other hand, in order to avoid the problem resulting from an iron silicate slag, a process is used as a batch, and once interrupt blowing for the state where a white regulus and a slag live together, a furnace is made to \*\*\*\*, a slag is discharged, it leaves in convertor of only a white regulus, and oxidization to crude copper is performed. This method includes the various disadvantageous profits resulting from a batch method, and makes convertor operation complicated.

[0016] By the Mitsubishi continuation copper-metallurgy method, the deposit of a magnetite is avoided by using a calcium ferrite slag at a convertor (C furnace) process, and crude copper is continuously manufactured from the about [ MG65% ] mat. However, there were the following problems resulting from a calcium ferrite slag.

[0017] (1) The copper grace in a slag changes continuously to oxygen tension, and the copper grace in a slag becomes high, so that S grace in crude copper is lowered. Practically, it is not efficient from the point of copper yield for Cu in a slag to become 13 - 15% at about 0.5 - 1%, and to make S in crude copper into S grace not more than this.

[0018] (2) Even if it dissolves chemically and anneals the copper content in a calcium ferrite slag mainly with an oxide, its recovery of the copper by sifting is low.

[0019] (3) As mentioned above,  $\text{SiO}_2$  in a calcium ferrite slag If it becomes about 1 - 3%, viscosity will increase remarkably and foaming (foaming) will be started. For this reason, the mat which the iron silicate slag mixed was difficult to use it as a raw material.  $\text{SiO}_2$  which can permit mixing into a mat if Fe grace in a mat is made into 10% To the mat, it is 0.2% or less and needed to be cautious of especially mixing prevention of the slag to the mat produced from a mat refining process.

[0020] (4) For a low reason, Pb is hard to be distributed into a slag and the solubility of Pb condenses to crude copper. For this reason, manufacture of the anode which can be electrolyzed by the conventional method from a high Pb raw material was difficult.

[0021] (5) When the same temperature compares, since the permeability to brick is large, the corrosion nature of convertor brick is larger than a silicate slag.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] When oxidizing a copper sulfide mineral concentrate or a mat continuously and obtaining a white regulus or crude copper by the method of this invention, There is no magnetite trouble and it is SiO<sub>2</sub>. It is applicable also to processing of the copper sulfide mineral concentrate and mat to contain, and there is little loss of the copper to a slag, and recovery of the copper content in the slag by flotation is possible, the removal ability to the slag of As, Sb, and Pb is high, and refining of a copper sulfide mineral concentrate with little \*\*\*\* of brick can be performed.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] When oxidizing a copper sulfide mineral concentrate or a mat continuously and obtaining a white regulus or crude copper, the purpose of this invention (1) There is no magnetite trouble at the usual copper refining temperature of 1300 degrees C or less. (2) SiO<sub>2</sub> Can apply also to processing of the copper sulfide mineral concentrate and mat to contain, there is little loss of the copper to (3) slags, and recovery of the copper content in a slag is possible by (4) flotation. (5) The removal ability to the slag of As, Sb, and Pb is high, and is to offer the refining method of a copper sulfide mineral concentrate with little \*\*\*\* of (6) bricks.

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## MEANS

[Means for Solving the Problem] The method of this invention is  $\text{SiO}_2$  as a solvent to a copper sulfide mineral concentrate. It is characterized by carrying out oxidization refining so that the mat near the slag and white regulus whose weight ratios of  $\text{Fe}/(\text{FeOx}+\text{SiO}_2+\text{CaO})$  a source and the source of  $\text{CaO}$  are added, and the weight ratios of  $\text{CaO}/(\text{SiO}_2+\text{CaO})$  are 0.3-0.6, and are 0.2-0.5, a white regulus, or crude copper may be generated.

[0024] Moreover, it is  $\text{SiO}_2$  to the mat obtained by carrying out refining of the copper sulfide mineral concentrate. It is characterized by carrying out oxidization refining so that the slag and crude copper whose weight ratios of  $\text{Fe}/(\text{FeOx}+\text{SiO}_2+\text{CaO})$  a source and the source of  $\text{CaO}$  are added, and the weight ratios of  $\text{CaO}/(\text{SiO}_2+\text{CaO})$  are 0.3-0.6, and are 0.2-0.5 may be generated.

[0025] The iron calcium silicate slag which uses the feature of the slag in the high oxygen tension conditions which manufacture a white regulus or crude copper by the iron silicate slag conventionally used by copper refinement, the calcium ferrite slag used by the Mitsubishi method, and this invention is compared, and is shown in Table 1.

[0026]

[Table 1]

	鉄シリケート スラグ	カルシウムフェラ イトスラグ	鉄カルシウムシリ ケートスラグ
粘性が低い	×	○	○
マット、粗銅の 懸垂が少ない	×	○	○
銅の酸化溶解が 少ない	×	×	○
銅の硫化溶解が 少ない	○	×	×
Pbの溶解度が 高い	○	×	○
As, Sb溶解度	×	○	○
Mg 衬付溶解度	×	○	○
煉瓦の熔損が 少ない	○	×	○

[0027] Adding some  $\text{CaO}$  to an iron silicate slag, and improving viscosity conventionally, has been performed. However, at the mat refining process, if  $\text{CaO}$  grade becomes high, since the solubility as a copper sulfide will increase and also the amount of slags will also increase, it has been thought that it is disadvantageous. however, under the conditions which coexist with the white regulus from which the sulfuration dissolution does not pose a problem, or crude copper With the iron calcium silicate slag used by this invention, to copper oxidizing melting increasing remarkably in an iron silicate slag or a calcium ferrite slag Since there is little copper oxidizing melting and it ends, if the amount of losses of the copper by amount of slags  $\times$  copper grade = oxidizing melting estimates It found out becoming less than a conventional method (the mat refining method, white regulus refining, and the direct copper-metallurgy method of high MG using an iron silicate slag or a calcium ferrite slag), and resulted in this invention.

[0028] Drawing 1 is the graph which showed the copper grade (C) in the copper quantity in the 1300-degree C slag in the case of oxidizing a copper sulfide mineral concentrate and obtaining the mat of MG75 (A), the amount of slags (B) to generate, and a slag to the weight ratio (horizontal axis) of  $\text{CaO}/\text{in a slag } (\text{SiO}_2+\text{CaO})$ , and Fe% (vertical axis). The saturation line of each solid phase is shown in each drawing, and the weight ratios of  $\text{CaO}/(\text{SiO}_2+\text{CaO})$  are 2  $\text{CaO}-\text{SiO}_2$  or more in 0.6. It deposits. Moreover, if Fe

grace is too high, a magnetite deposits. The left end of drawing is equivalent to the conventional iron silicate slag ( $\text{CaO}=0\%$ ). [0029] It is in the inclination for copper grace to become low, so that the iron grace in a slag becomes low, and copper grace becomes low, so that the weight ratio of  $\text{CaO}/(\text{SiO}_2+\text{CaO})$  is large. The amount of slags decreases, so that the iron grace in a slag is high, since the amount of slags to generate is decided by iron grace in a slag and \*\*\*\* which should be removed is decided with a raw material. As the copper quantity (the amount of losses) which shifts to a slag is decided by copper grace in an amount of slags x slag and was shown in the best stage, 0.5 to 0.6 and the weight ratio of  $\text{Fe}/(\text{FeOx}+\text{SiO}_2+\text{CaO})$  have [ the weight ratio of  $\text{CaO}/(\text{SiO}_2+\text{CaO})$  ] the minimal value near composition of 0.2-0.5. Namely, what is necessary is just to choose the slag of composition of this neighborhood from the point of making loss of the copper to the inside of a slag into the minimum.

[0030] On the other hand, drawing 2 is the graph which showed the activity coefficient of As in a slag to slag composition. The weight ratio of  $\text{CaO}/(\text{SiO}_2+\text{CaO})$  is shown in the horizontal axis, and the activity coefficient ( $\gamma_{\text{AsO}1.5}$ ) of As is shown in the vertical axis. The iron silicate slag of the former [ left end / of drawing ] and a right end are equivalent to a calcium ferrite slag, and the iron calcium silicate slag used by this invention is located in both middle. An activity coefficient shows that the element is easy to be removed in a slag, so that a value is small.

[0031] From drawing 2, when the weight ratio of  $\text{CaO}/(\text{SiO}_2+\text{CaO})$  is made or more into 0.3, a bird clapper understands the removal ability of As more highly than an iron silicate slag. In addition, behavior with the same said of Sb belonging to the same V group as As is shown.

[0032] On the other hand, as shown in drawing 3, Pb shows reverse behavior, and the activity coefficient ( $\gamma_{\text{PbO}}$ ) of Pb serves as a remarkable big value by the calcium ferrite slag, and shows forge-fire small \*\*\*\*\* with the small weight ratio of  $\text{CaO}/(\text{SiO}_2+\text{CaO})$ . Although the removal ability of Pb is a little inferior in the weight ratio of  $\text{CaO}/(\text{SiO}_2+\text{CaO})$  by 0.3-0.6 compared with an iron silicate slag, compared with the calcium ferrite slag, it has quite big removal ability.

[0033] As mentioned above, a bird clapper is known that it is easy to remove in a slag about both As Sb and Pb by setting the weight ratio of  $\text{CaO}/(\text{SiO}_2+\text{CaO})$  to 0.3-0.6.

[0034] Drawing 4 shows the same relation as drawing 1 about the case where the crude copper of about 1 - 1.5% of S grace is obtained under white regulus coexistence. The left end of drawing is equivalent to an iron silicate slag ( $\text{CaO}=0\%$ ), and a right end is equivalent to a calcium ferrite slag ( $2 = 0\%$  of  $\text{SiO}(s)$ ). From drawing of the best stage, the copper amount of losses is 2  $\text{CaO-SiO}_2$ . It turns out that the minimum is taken in the place near a saturation line. Although the copper amount of losses also has comparatively few calcium ferrite slags, it is little  $\text{SiO}_2$ . When carried in, it is 2  $\text{CaO-SiO}_2$ . It becomes saturation and the problem of foaming of a slag is produced.

[0035] About distribution of an impurity, a calcium ferrite slag cannot absorb Pb easily, to there being a fault of being hard to absorb As and Sb, is setting the weight ratio of  $\text{CaO}/(\text{SiO}_2+\text{CaO})$  to 0.3-0.6, and becomes easy to be in the same inclination as mat refining, and to remove both As Sb and P in a slag in an iron silicate slag.

[0036] As mentioned above, it turns out that there is the optimal composition whose weight ratio of  $\text{CaO}/(\text{SiO}_2+\text{CaO})$  the weight ratio of 0.3 to 0.6 and  $\text{Fe}/(\text{FeOx}+\text{SiO}_2+\text{CaO})$  carries out copper loss to the range of 0.2-0.5 at the minimum, and tends to remove both Pb As and Sb.

[0037] Drawing 5 is what showed the copper grace in the slag to oxygen tension, and the behavior in the case of obtaining the low crude copper of S grace in the field where the degree of oxidization is still higher is shown from the case where it is shown in drawing 4. The inside of drawing and Curve A show the iron calcium silicate slag which an iron silicate slag and Curve D use by the calcium ferrite slag, and Curves B and C use by this invention. In an iron silicate slag and a calcium ferrite slag, the copper in a slag changes continuously to 100% according to elevation of oxygen tension. Since it becomes copper-oxide saturation by about 20% of copper grace with an iron calcium silicate slag to it, the copper grace in a slag does not go up more than this grace. That is, if crude copper is made from this condition, 0.01% or less of crude copper (crude copper of copper-oxide saturation) will be obtained [ the copper grace in a slag ] for S grace at about 20%. If the crude copper of the degree of oxidization of the same grade is made from an iron silicate slag or a calcium ferrite slag, the copper grace in a slag will become remarkably high, and will not serve as practical use from the point of yield.

[0038] About the corrosion of brick, osmosis in the brick of a slag component is considered to do big influence. Usually, when a slag component permeates into the magnesite chrome brick used by copper refinement, it is known that the iron oxide in a slag will be absorbed by the spinel containing a periclase ( $\text{MgO}$ ) or  $\text{Cr}_2\text{O}_3$ .  $\text{SiO}_2$  When it permeates into brick in the case of the included slag, and an iron oxide dissolves in a periclase ( $\text{MgO}$ ) or a spinel, it is  $\text{SiO}_2$  in a slag. Concentration becomes high. Consequently, the viscosity of a slag goes up and it is thought that the slag osmosis beyond it is suppressed.

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## EXAMPLE

[Example] [Example 1] Melting mat 40g and 60g of molten slags shown in Table 2 are prepared in the crucible made from a magnesia held at 1300 degrees C, a lance pipe is used for the copper sulfide mineral concentrate of the composition shown in Table 2 the same during a melting bath, and SiO<sub>2</sub> (SiO<sub>2</sub> pure 95% or more per part) and CaO (CaO pure 98% or more per part), and it is in 95%O<sub>2</sub>-5% N<sub>2</sub> (capacity %). The lance pipe was blown without being immersed.

[0040]

[Table 2]

(重量%)

	Cu	Fe	S	SiO <sub>2</sub>	CaO
熔融マット	74.8	2.0	20.5	—	—
熔融スラグ	2.4	35.1	—	22.9	16.2
硫化銅精鉱	31.4	24.0	30.2	6.9	—

[0041] The lance pipe used for the entrainment is a product made from an alumina, and blew 20gSiO<sub>2</sub> for copper sulfide mineral concentrate and 1.94g/for /, and 2.20gCaO for /with 95%O<sub>2</sub>-5%N<sub>2</sub> (capacity %) gas for 4.5l/.

[0042] After continuing an entrainment for 50 minutes on condition that the above and standing it still for 10 minutes, cooling solidification is carried out, a mat and the weight row of a slag are asked for analysis grace, each amount of components is deducted from grace in the mat inserted in first and the amount row of a slag, and the result which calculated the grace in the amount of mats generated by the reaction and the amount row of slags is shown in Table 3.

[0043]

[Table 3]

(重量%)

	産出重量 (g)	Cu	Fe	S	SiO <sub>2</sub>	CaO
生成マット	375	76.2	1.0	20.1	—	—
生成スラグ	641	1.9	35.0	—	23.8	16.0

[0044]

[Example 2] 30g of melting crude copper and 80g of molten slags of the composition shown in Table 4 are prepared in the crucible made from a magnesia held at 1300 degrees C, a lance pipe is used for the copper sulfide mineral concentrate of the composition shown in Table 4 the same during a melting bath, and SiO<sub>2</sub> (SiO<sub>2</sub> pure 95% or more per part) and CaO (CaO pure 98% or more per part), and it is in 95%O<sub>2</sub>-5% N<sub>2</sub> (capacity %). The lance pipe was blown without being immersed.

[0045]

[Table 4]

(重量%)

	Cu	Fe	S	SiO <sub>2</sub>	CaO
熔融粗銅	97.5	—	1.2	—	—
熔融スラグ	3.8	31.0	—	26.1	18.2
硫化銅精鉱	31.4	24.0	30.2	6.9	—

[0046] The lance pipe used for the entrainment is a product made from an alumina, and blew 20gSiO<sub>2</sub> for copper sulfide mineral concentrate and 3.02g/for /, and 2.88gCaO for /with 95%O<sub>2</sub>-5%N<sub>2</sub> (capacity %) gas for 5.8l/.

[0047] After continuing an entrainment for 50 minutes on condition that the above and standing it still for 10 minutes, cooling

solidification is carried out, crude copper and the weight row of a slag are asked for analysis grace, each amount of components is deducted from grace in the crude copper and the amount row of a slag which were inserted in first, and the result which calculated the grace in the amount of crude copper generated by the reaction and the amount row of slags is shown in Table 5.

[0048]

[Table 5]

(重量%)

	産出重量 (g)	Cu	Fe	S	SiO <sub>2</sub>	CaO
生成粗銅	273	98.1	—	0.99	—	—
生成スラグ	764	4.2	29.8	—	26.3	17.9

[0049]

[Example 3] 60g of melting crude copper and 40g of molten slags of the composition shown in Table 6 were prepared in the crucible made from a magnesia held at 1300 degrees C, and the mat of the composition shown in Table 6 the same during a melting bath, and SiO<sub>2</sub> (SiO<sub>2</sub> pure 95% or more per part) and CaO (CaO pure 98% or more per part) were blown with 95%O<sub>2</sub>-5% N<sub>2</sub> (capacity %), without immersing a lance pipe.

[0050]

[Table 6]

(重量%)

	Cu	Fe	S	SiO <sub>2</sub>	CaO
溶融粗銅	97.5	—	1.2	—	—
溶融スラグ	18.4	25.3	—	22.1	13.5
マット	65.3	9.7	21.4	—	—

[0051] The lance pipe used for the entrainment is a product made from an alumina, and is 20gSiO<sub>2</sub> for copper sulfide mineral concentrate and 1.78g/for /. 1.14gCaO for /was blown with 95%O<sub>2</sub>-5%N<sub>2</sub> (capacity %) gas for 4.0l./.

[0052] After continuing an entrainment for 50 minutes on condition that the above and standing it still for 10 minutes, cooling solidification is carried out, crude copper and the weight row of a slag are asked for analysis grace, each amount of components is deducted from grace in the crude copper and the amount row of a slag which were inserted in first, and the result which calculated the grace in the amount of crude copper generated by the reaction and the amount row of slags is shown in Table 7.

[0053]

[Table 7]

(重量%)

	産出重量 (g)	Cu	Fe	S	SiO <sub>2</sub>	CaO
生成粗銅	558	98.8	—	0.05	—	—
生成スラグ	382	20.6	24.9	—	20.8	14.0

[0054] In the examination of these examples 1-3, the dust incidence rate was 4 - 7% of the weight of a range. In the meantime, there was no trouble by generating of a magnetite.

[0055]

[Example 4] The slag generated in the example 3 was pulverized with the ball mill until the 200-mesh undershirt became 95%, this slag 200g was made into the slurry 65% of the weight with water, and the flotation test was carried out with the flotation machine for an examination. Under the present circumstances, DM-2000 of marketing, MCB-4, and 0.006g of 0.01g of 0.03g of xanthates were respectively added as 0.02g of pine oils, and a flotation reagent as a frothing agent.

[0056] A test result is shown in Table 8. It was checked that 80% or more of copper is recoverable with flotation.

[0057]

[Table 8]

原鉱	精鉱		尾鉱	
Cu%	Cu%	分布	Cu%	分布
20.8	38	81	1.5	19



[0058]

[Example 5] Oxygen-enrichment air of 50% of a mineral concentrate burner to oxygen in which what prepared the mineral concentrate, powder silica, and powder lime (what ground all to 200 micrometers or less) of composition which were shown in Table 9 by the predetermined ratio, and was dried using small self-\*\*\*\* with the bore of 1.5m of a reactor, a height of 3.5m, a bore [ of the settler section / of 1.5m ], and a length of 5.2m (henceforth \*\*\*\*) was prepared by the reactor ceiling. It blew in into the reactor and the slag and the mat were obtained. The fuel oil burner is included in the mineral concentrate burner, and the amount of fuel oils was adjusted so that the heat balance of a reactor might be maintained. Operation was performed for four days. The obtained result is shown in Table 9. Table 9 shows that the high-definition mat of MG 76 [ about ] was obtained stably.

[0059]

[Table 9]

(重量%)

		物量 (kg/h)	Cu	Fe	S	SiO <sub>2</sub>	CaO
処理	硫化銅精鉱	1040	31.4	25.1	30.2	6.9	—
	珪石	104	—	2	—	95	
	石灰石	208	—	—	—	—	53
産出	熔融マット	382	76.8	1.0	20.1	—	—
	熔融スラグ	700	2.5	35.0	—	24.2	16.1

精鉱バーナー送風空気量 5 8 0 Nm<sup>3</sup> /h、酸素濃度 5 0 %、

重油量 5 3 リットル/h、

生成スラグ平均温度 1 2 5 8℃、生成マット平均湿度 1 1 4 6℃

[0060]

[The example 1 of comparison] Melting mat 30g of the composition shown in Table 10 and 40g of molten slags were prepared in the crucible made from a magnesia held at 1300 degrees C, and the copper sulfide mineral concentrate of the composition shown in Table 10 the same during a melting bath and SiO<sub>2</sub> (SiO<sub>2</sub> pure 97% or more per part) were blown with 95%O<sub>2</sub>-5% N<sub>2</sub> (capacity %), without immersing a lance pipe.

[0061]

[Table 10]

(重量%)

	Cu	Fe	S	SiO <sub>2</sub>	CaO
熔融マット	76.3	2.8	20.8	—	—
熔融スラグ	5.0	42.0	—	30.0	—
硫化銅精鉱	30.3	29.1	33.5	1.8	—

[0062] The lance pipe used for the entrainment is a product made from an alumina, and is 37.5gSiO<sub>2</sub> for copper sulfide mineral concentrate and 7.6g/for /. It blew in with 95%O<sub>2</sub>-5%N<sub>2</sub> (capacity %) gas for 9.2l./.

[0063] After [ of a test start ] 5 minutes, by formation of the high-melting point matter which the generation magnetite mixed with the mat, the entrainment to the inside of the melt of a feed became impossible, and further, for these matter, lock out of a lance pipe took place and it became uncontinuable [ an experiment ].

[0064]

[The example 2 of comparison] 60g of melting crude copper and 40g of molten slags of the composition shown in Table 11 were prepared in the crucible made from a magnesia held at 1300 degrees C, and the mat and CaO (CaO pure 98% or more per part) of the composition shown in Table 11 the same during a melting bath were blown with 95%O<sub>2</sub>-5% N<sub>2</sub> (capacity %), without immersing a lance pipe.

[0065]

[Table 11]

(重量%)

	Cu	Fe	S	SiO <sub>2</sub>	CaO
溶融粗銅	97.5	—	1.2	—	—
溶融スラグ	16.4	47.6	—	—	17.6
マット	64.0	9.5	21.0	2.0	—

[0066] The lance pipe used for the entrainment is a product made from an alumina, and blew 20g mat for /, and 0.73gCaO for /with 95%O<sub>2</sub>-5%N<sub>2</sub> (capacity %) gas for 0.20l/.

[0067] The boiling phenomenon of a slag happened after [ of a test start ] 30 minutes, the great portion of \*\*\*\* in a crucible boiled over out of the crucible, and it became uncontinuable [ an experiment ].

[0068]

[The example 3 of comparison] 60g of melting crude copper and 40g of molten slags of the composition shown in Table 12 were prepared in the crucible made from a magnesia held at 1300 degrees C, and the mat and CaO (CaO pure 98% or more per part) of the composition shown in Table 12 the same during a melting bath were blown with 95%O<sub>2</sub>-5% N<sub>2</sub> (capacity %), without immersing a lance pipe.

[0069]

[Table 12]

(重量%)

	Cu	Fe	S	SiO <sub>2</sub>	CaO
溶融粗銅	97.5	—	1.2	—	—
溶融スラグ	16.4	47.6	—	—	15.7
マット	65.3	9.7	21.4	—	—

[0070] The lance pipe used for the entrainment is a product made from an alumina, and blew 20g mat for /, and 0.7gCaO for /with 95%O<sub>2</sub>-5%N<sub>2</sub> (capacity %) gas for 4.2l/.

[0071] After continuing an entrainment for 50 minutes on condition that the above and standing it still for 10 minutes, cooling solidification is carried out, crude copper and the weight row of a slag are asked for analysis grace, each amount of components is deducted from grace in the crude copper and the amount row of a slag which were inserted in first, and the result which calculated the grace in the amount of crude copper generated by the reaction and the amount row of slags is shown in Table 13.

[0072] Although the crude copper of 0.06% of S grace was obtained, the copper grace in a slag was high and the yield of crude copper was about 80%.

[0073]

[Table 13]

(重量%)

	産出重量 (g)	Cu	Fe	S	SiO <sub>2</sub>	CaO
生成粗銅	534	98.3	—	0.06	—	—
生成スラグ	290	32.7	32.0	—	—	11.2

[0074]

[The example 4 of comparison] The calcium ferrite slag containing Cu16.4%, Fe47.6%, and CaO15.7% was pulverized with the ball mill until the 200-mesh undershirt became 95%, this slag 200g was made into the slurry 65% of the weight with water, and the flotation test was carried out with the flotation machine for an examination. Under the present circumstances, DM-2000 of marketing, MCB-4, and 0.006g of 0.01g of 0.03g of xanthates were respectively added as 0.02g of pine oils, and a flotation reagent as a frothing agent.

[0075] A test result is shown in Table 14. It was difficult to collect copper from a calcium ferrite slag with flotation.

[0076]

[Table 14]

原鉱	精鉱		尾鉱	
Cu%	Cu%	分布	Cu%	分布
16.4	21	54	10	46

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[Translation done.]

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3. In the drawings, any words are not translated.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] They are the copper quantity in the 1300-degree C slag in the case of oxidizing a copper sulfide mineral concentrate and obtaining the mat of MG75 (A), the amount of slags (B) to generate, and the graph which showed the copper grace in a slag (C) to  $\text{CaO} / (\text{SiO}_2 + \text{CaO})$  ratio in a slag (horizontal axis), and Fe% (vertical axis).

[Drawing 2] It is the graph which showed the activity coefficient of As in a slag to slag composition.

[Drawing 3] It is the graph which showed the activity coefficient of Pb in a slag to slag composition.

[Drawing 4] It is the graph which showed the copper grace (C) in the copper quantity in the 1300-degree C slag in the case of obtaining the crude copper of about 1 - 1.5% of S grace (A), the amount of slags (B) to generate, and a slag to  $\text{CaO} / (\text{SiO}_2 + \text{CaO})$  ratio in a slag (horizontal axis), and Fe% (vertical axis) under white regulus coexistence.

[Drawing 5] In 1573K, it is the graph which shows the relation between copper concentration and oxygen tension which carries out oxidizing melting to a slag under \*\*\*\* coexistence.

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[Translation done.]

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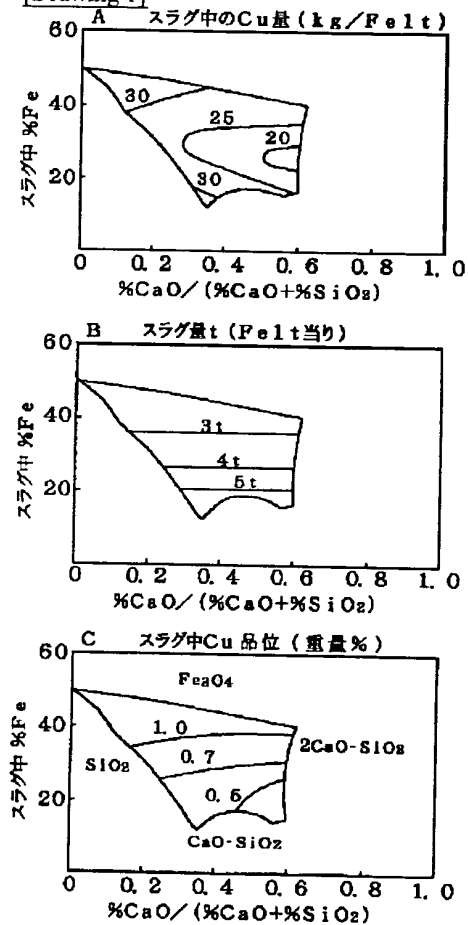
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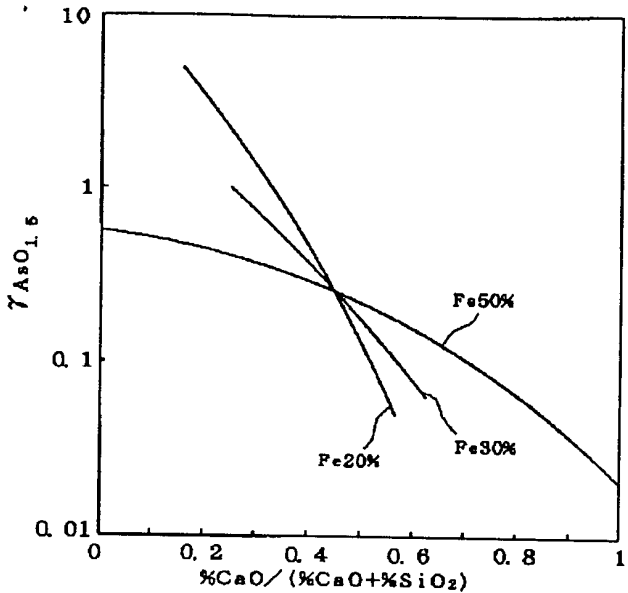
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DRAWINGS

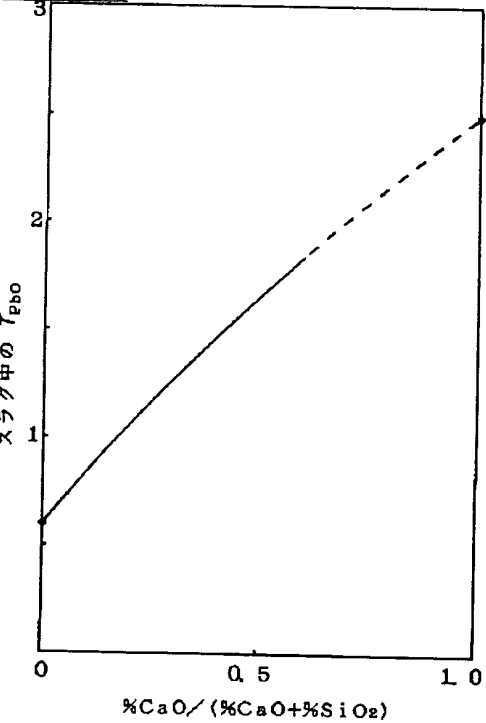
[Drawing 1]



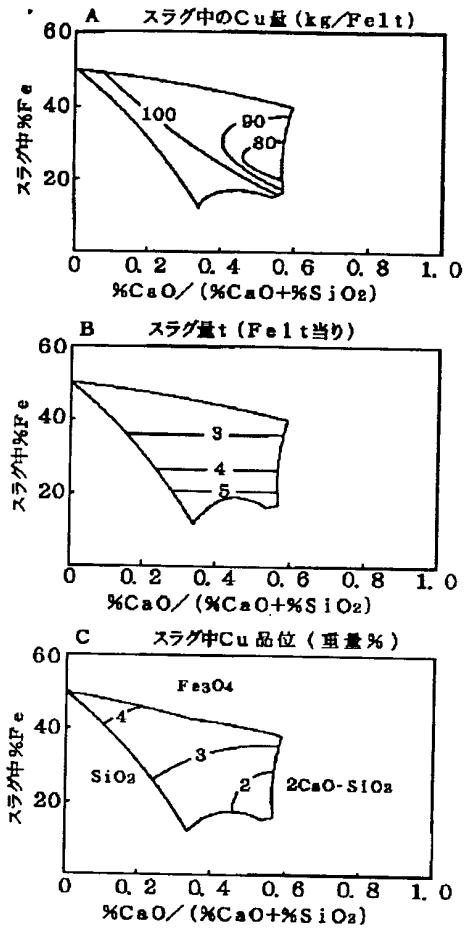
[Drawing 2]



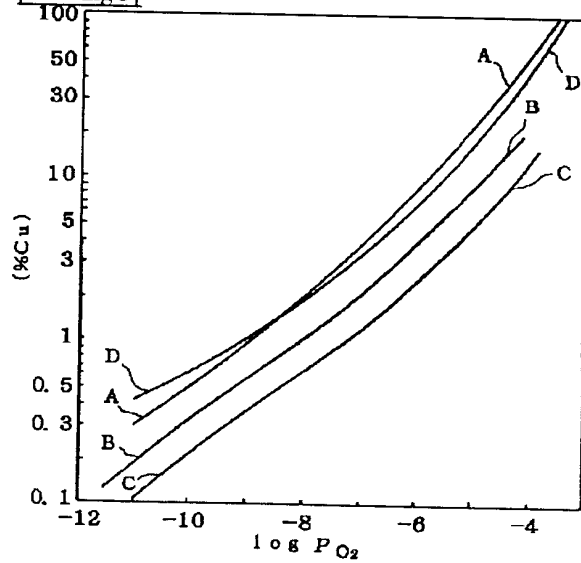
[Drawing 3]



[Drawing 4]



[Drawing 5]



[Translation done.]